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EXTREME PRESSURE LUBRICANT TESTS WITH PRETREATED TEST-PIECES.*

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Summary.

Experiments with the Timken and Four-Ball lubricant testing machines are described, in which considerable increases in the breakdown loads of doped and undoped oils were obtained by pretreatment of the test-pieces with chlorinated or sulphurized dope or with hydrochloric acid. Running-in tests showed that the layer so formed was not removed by running under loads below the breakdown load. The pretreatment of the Cornell (or Falex) test-pieces had no apparent effect, but when these were hardened to a value comparable with that of the other machines, the breakdown loads became too high for the machine to measure. The formation of the layers is discussed briefly.

Introduction.

In the course of work on the production and testing of extreme pressure lubricants, experiments were carried out on three well-known lubricant-testing machines to investigate the formation of the film on bearing surfaces which is believed to underlie the phenomena of E.P. lubrication. The results, as is common with machines of this type, are not entirely self-consistent, but are considered to be of sufficient interest to justify publication.

The machines used were the Timken, the Four-Ball, and the Cornell (or Falex).

Timken Machine.

The work was commenced with the Timken machine.[1]

The test-pieces consist of a flat-rimmed cylindrical cup approximately 2 inches in diameter rotating at 800 r.p.m. in contact with a flat steel block. The block is pressed against the cup by means of a lever system which multiplies the thrust ten-fold, the results usually being given in terms of the weight applied to the load lever. The standard test procedure consists of starting the motor and applying the load at the rate of approximately 2 lb. per second. The machine is then allowed to run for 10 minutes under a constant load, a gallon of the lubricant being circulated over the test-pieces throughout the run. The test is repeated at various loads until the maximum load which gives a smooth scar on the test-block is found.

Types of Scar Obtained with Timken Machine.

Under the above conditions the results obtained at low loads are a smooth scar (Fig. 1) or a breakdown (Fig. 2). At high loads (50–100 lb.), breakdown, if it occurs, is more severe (Fig. 3), and other types of scars may also be obtained; these are narrow and rough (Fig. 4), wide and scored (Fig. 5), or wide and smooth (Fig. 6). Inspection of the test-cups

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corresponding to Figs. 5 and 6 would reveal traces of metal "pick-up" indicating that a breakdown must have occurred during the run, although this was not indicated by a slowing down of the machine. It is clear, however, that the breakdown has been followed by recovery, since the damage to the surfaces has been repaired, the signs of breakdown being more obvious in Fig. 5 than in Fig. 6. When a severe breakdown, such as that shown in Fig. 3, takes place, the machine is slowed down considerably and the motor has to be stopped to avoid damage. The factors controlling the severity of breakdown cannot be said to be fully understood.

Rough scars, such as that shown in Fig. 4, were always accompanied by an appreciable darkening of the cup, which also became marked with circular lines parallel to its edge. Although completely satisfactory lubrication was not maintained, a high load was carried without the extensive damage to the test-pieces which accompanies a breakdown (Fig. 3).

The occurrence of these scars depended to some extent on the method of loading. Rapid application (*i.e.*, in less than 3 seconds) of a load of 100 lb. could produce a breakdown (Fig. 3) with most lubricants. Slower application might produce breakdown, breakdown followed by recovery (Figs. 5 and 6) or a narrow rough scar (Fig. 4). Very slow application (*i.e.*, in a time greater than 60 seconds) usually produced a narrow rough scar.

The changes in weight of the test-pieces accompanying the production of these types of scar are given in Table I. The oil used consisted of a mineral oil with a viscosity of 60 Redwood No. 1 seconds at 200° F. containing 2 per cent. of chlorine in the form of a chlorine-containing dope.

TABLE I.

Timken Machine—10-minute Tests on Doped Oil.

Load, lb.	Type of Scar.	Change in Weight of	
		Cup, mgm.	Block, mgm.
40	Smooth (Fig. 1)	− 8	− 1
100	Breakdown (Fig. 3)	+85	−232
100	Wide scored (Fig. 5)	+34	−109
100	" " (Fig. 6)	− 8	− 2
100	Rough (Fig. 4)	−88	+ 4

Experiments with Previously Used Cups.

It was clear that the production of the narrow, rough scars was connected with the above-mentioned changes in the surface of the cup, and it appeared that these at least began to occur during the application of the load. Tests were therefore carried out by applying the load before starting the motor; this had the expected effect of causing a marked reduction in the load carried by the doped and undoped oils, and also eliminated both the wide scars showing signs of recovery (Figs. 5 and 6) and the narrow, rough scars.

When rough scars were obtained in 10-minute tests under a load of

100 lb. with the standard method of loading, the cup suffered an appreciable loss in weight, as shown in Table I. This, however, did not correspond to a change in diameter of more than 0·01 mm. (*i.e.*, 0·02 per cent.) and it was therefore possible to use the cups again for further tests. This was done with both doped and undoped oils, and the results are given below in Table II.

TABLE II.

Timken Machine—10-minute Tests on Cups Previously Used at a Load of 100 lb. in Doped Oil.

Oil.	Load Applied.	State of Cup.	Maximum Load Withstood without Breakdown, lb.	Appearance of Scar.
Undoped.	Standard method.	Unused.	11	Smooth.
		Used.	18	,,
		Used and washed in water.	19	,,
Undoped.	Before starting.	Unused.	6	Smooth.
		Used.	21	,,
		Used and washed in water.	20	,,
Doped.	Standard method.	Unused.	100	Rough.
		Used.	100	,,
		Used and washed in water.	100	,,
Doped.	Before starting.	Unused.	20	Smooth.
		Used.	100	Rough.
		Used and washed in water.	100	,,

It should be mentioned that some of the scars obtained under higher loads with these cups were somewhat severely scored. The scoring in this case was clearly due to the fact that the surface of the cup was lined after having been used to produce a rough scar. However, the scar was still quite narrow.

It is seen that in spite of the irregularity of the surfaces, the loads withstood by the used cups were in some cases markedly higher than that withstood with new cups. This change was believed to be connected with the darkening of the cup, which was most likely to be due to reaction between it and the dope contained in the oil.

Experiments with Cups Heated in Pure E.P. Lubricant.

Some cups were therefore heated in the dope itself (chlorinated type). Preliminary experiments showed that a uniform layer could be obtained on them by heating for 5 minutes at 200° C. In order to remove any dope retained after treatment, the hot cups were cooled in mineral oil and were then washed in trichlorethylene. It was found that the layer then left on the cup was readily deliquescent (Fig. 7*b*); some of the cups were therefore further washed in water and dried. The cups were all left under oil or covered with grease in the period between treatment and use.

The results obtained with cups treated in this way are given in Table III.

It is seen that the results obtained with those cups heated in the dope

TABLE III.

Timken Machine—10-minute Tests on Cups Previously Treated for 5 Minutes at 200° C. in Pure E.P. Lubricant.

Oil.	Load Applied.	State of Cup.	Maximum Load Withstood Without Breakdown, lb.	Appearance of Scar.
Undoped.	Standard method.	Untreated.	11	Smooth.
		Treated.	80	,,
		Treated and washed in water.	19	,,
Undoped.	Before starting.	Untreated.	6	Smooth.
		Treated.	79	Slightly scored.
		Treated and washed in water.	20	Smooth.
Doped.	Standard method.	Untreated.	100	Rough.
		Treated.	100	,,
		Treated and washed in water.	100	,,
Doped.	Before starting.	Untreated.	20	Smooth.
		Treated.	100	Rough.
		Treated and washed in water.	58	Smooth.

were again higher than those obtained with the untreated cups, the figures obtained with those which had not been washed in water being particularly high. The scars obtained when breakdown did not occur were narrow

TABLE IV.

Timken Machine—Tests of Two Types to Determine the Maximum Load Withstood after Running-in for 1 Hour.

(a) One 10-minute run with the run-in cup on a new block-face.
(b) A series of 2-minute runs with the same run-in cup and a new block-face each time, the load being increased in steps of 2 lb.

Oil.	State of Cup.	Load during Running-in, Applied by Standard Method, lb.	Tests after Running-in.			
			Type.	Load Applied.	Maximum Load Withstood without Breakdown, lb.	Appearance of Scar.
Undoped.	Untreated.	5	a	Standard method.	10	Smooth.
		5	a	Before starting.	10	,,
	Treated.	15	a	Standard method.	46	Smooth.
		15	a	Before starting.	50	,,
		15	b	,, ,,	42	,,
	Treated and washed in water.	15	a	Standard method.	50	Smooth.
		15	a	Before starting.	35	,,
		15	b	,, ,,	26	,,
Doped.	Untreated.	33	a	Before starting.	60	Smooth.
	Treated.	50	a	,, ,,	100	Rough.
	Treated and washed in water.	50	a	,, ,,	100	,,

and quite smooth (Fig. 8) except at the higher loads, when roughening took place to an extent which was rather variable.

Some tests lasting for longer periods were also carried out with cups treated in this way, and the results are given in Table IV. These were all run-in for an hour, and were then used for two types of test. The first was to determine the breakdown load of the oil with a run-in cup, and the second to find the result of running-in with gradually increasing loads.

Increases in the load withstood by undoped oil with treated cups are again shown.

Experiments with Cups Treated with Hydrochloric Acid.

One of the most active products of the high-temperature decomposition of chlorinated dopes is hydrochloric acid, and some tests were therefore carried out with cups which had been treated with it. The cups were immersed in acid of ten normal strength at 50° C. for 5 minutes, followed by washing in water. The results are given in Table V, and will be seen to show the same tendency as those obtained with cups which had been treated with the dope.

TABLE V.

Timken Machine—Tests on Cups Treated for 5 Minutes at 50° C. in 10N·HCl and Washed in Water.

After running-in, only one 10-minute run was carried out on each cup.

Oil.	Conditions of Running-in (Standard Loading).	Load Applied.	Tests after Running-in.	
			Maximum Load Withstood without Breakdown, lb.	Appearance of Scar.
Undoped.	None.	Standard method.	19	Smooth.
	,,	Before starting.	20	,,
	1 hr. at 15 lb.	,, ,,	40	,,
Doped.	None.	Standard method.	100	Rough.
	,,	Before starting.	78	Partly rough.
	1 hr. at 15 lb.	,, ,,	100	Rough.

FOUR-BALL MACHINE.

In view of the well-known lack of agreement between the results given by different lubricant testing machines, similar experiments were also carried out with the Four-Ball machine. The test-pieces of this consist of ½-inch steel balls of ball-bearing quality; one of these is rotated at 1500 r.p.m. in contact with the other three, which are clamped together in a cup containing the lubricant under test. The load is applied before the commencement of the test, which is of 1 minute's duration.

Full descriptions of this machine are available elsewhere.[2, 3, 4] The breakdown load of a lubricant is found in terms of the load required to produce seizure 2½ seconds after the test is started,[5] and the maximum

load withstood for a minute can also be obtained.[3, 4] If the diameters of the scars on the three stationary balls at the end of each test are plotted against the load, it is also possible, with some oils, to determine the pressure at which lubrication is re-established after seizure. From Fig. 12 it will be seen that if double logarithmic paper is used, the lines representing constant pressure are straight. The graphs given therein

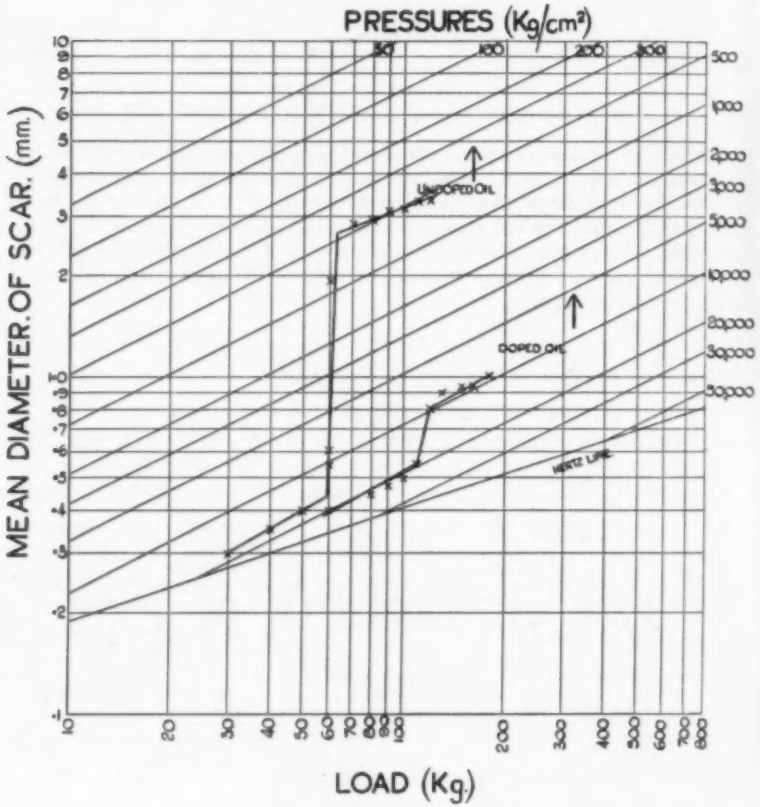

FIG. 9.

DIAMETER OF SCAR ON THE LOWER BALLS AFTER A TEST PLOTTED AGAINST THE LOAD. FOUR BALL MACHINE.

show that with both doped and undoped oils the diameter of the scar at loads too low to produce seizure is nearly the Hertz value for the elastic deformation of the balls. After seizure, which is marked by a sudden increase in the diameter of the scar, the graph is often parallel with the lines of constant pressure, indicating that over a range of loads the pressure at which lubrication is re-established after seizure is constant. At still

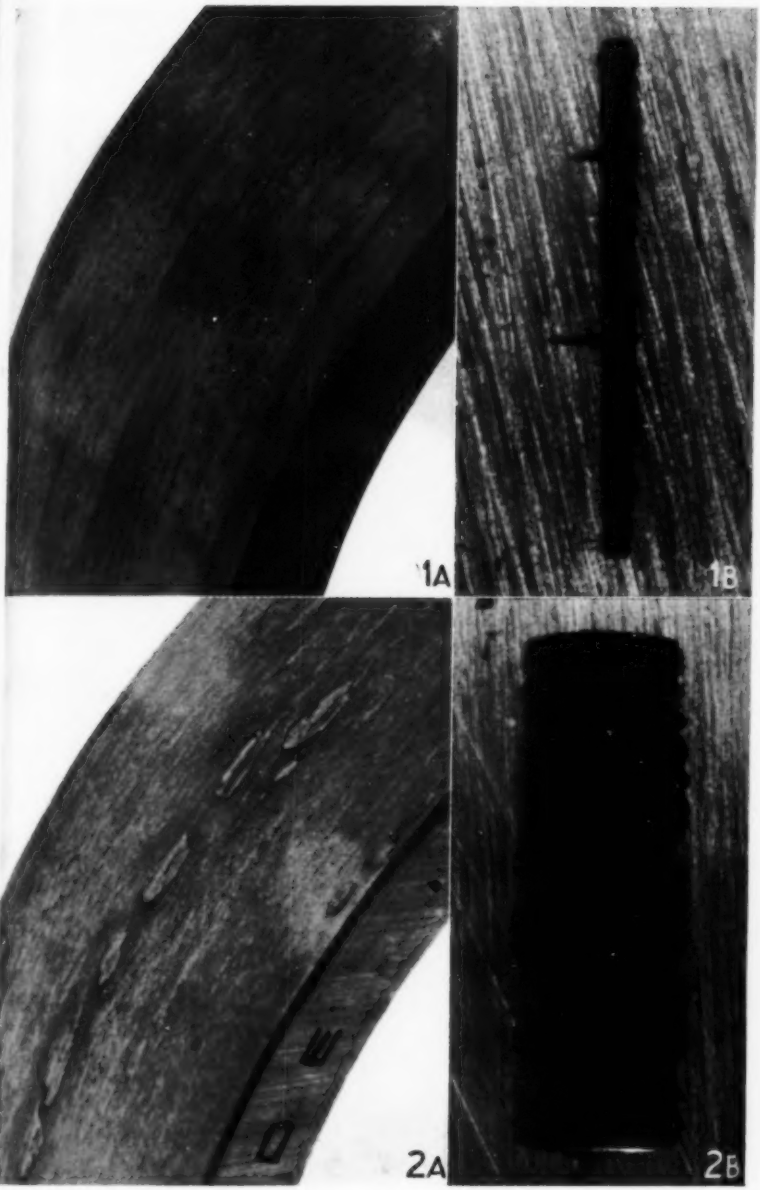

FIG. 1 (*a*) AND (*b*).

SMOOTH SCAR OBTAINED WHEN NO BREAKDOWN OCCURS AT LOW LOADS WITH A MINERAL OIL.

FIG. 2 (*a*) AND (*b*).

BREAKDOWN WITH A MINERAL OIL.

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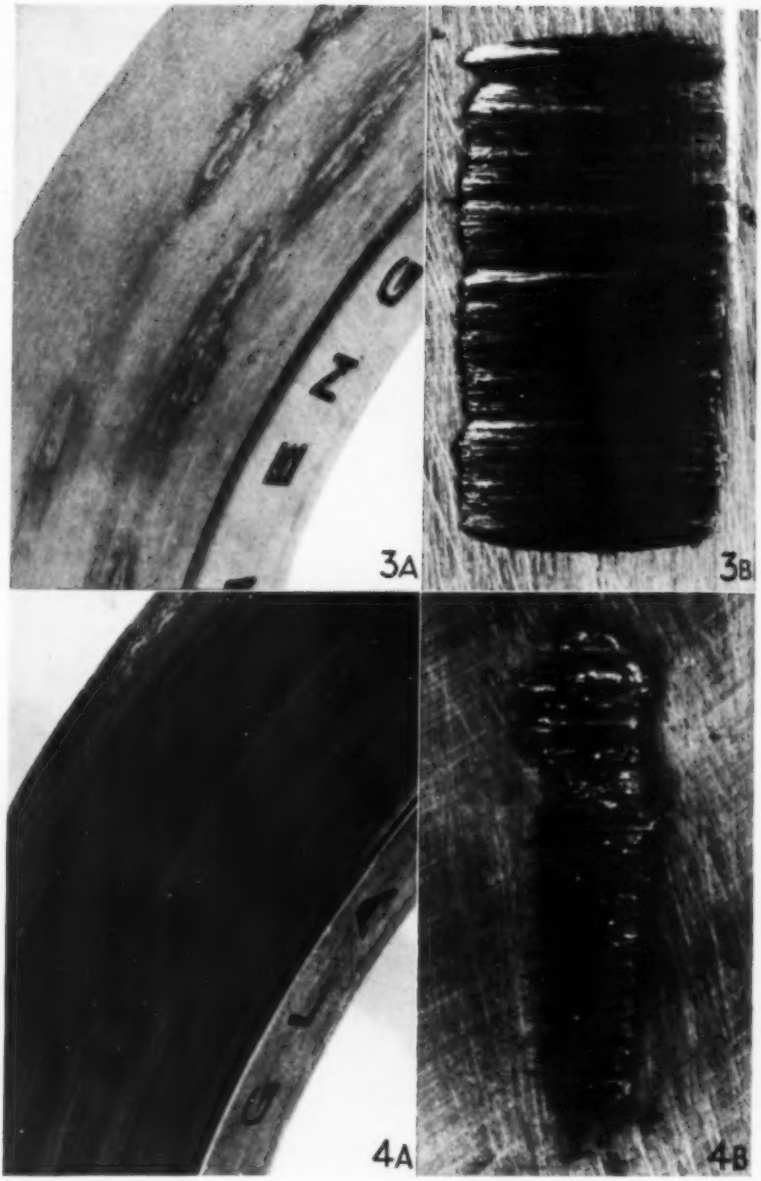

FIG. 3 (*a*) AND (*b*).

BREAKDOWN WITH DOPED OIL UNDER HIGH LOAD.

FIG. 4 (*a*) AND (*b*).

ROUGH SCAR OBTAINED WITH DOPED OIL UNDER 100 LB. LOAD

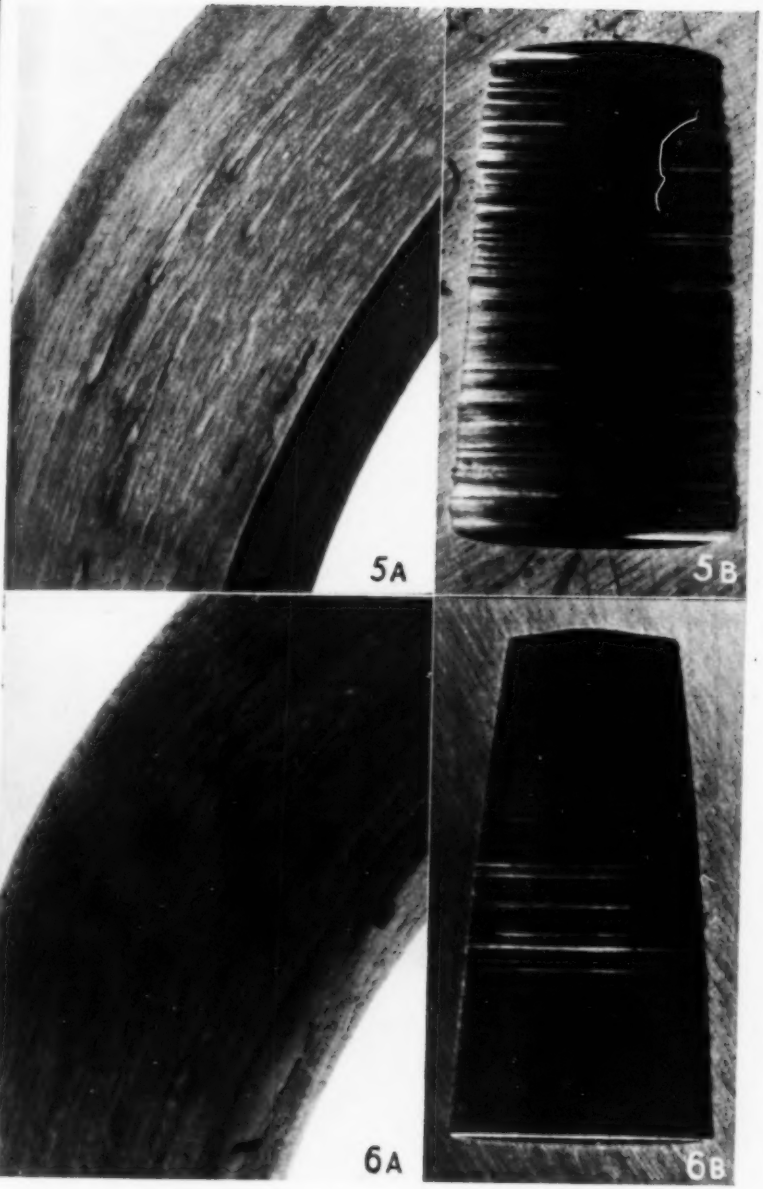

FIG. 5 (*a*) AND (*b*).
WIDE SCORED SCAR OBTAINED WITH DOPED OIL.

FIG. 6 (*a*) AND (*b*).
WIDE SMOOTH SCAR OBTAINED WITH DOPED OIL.

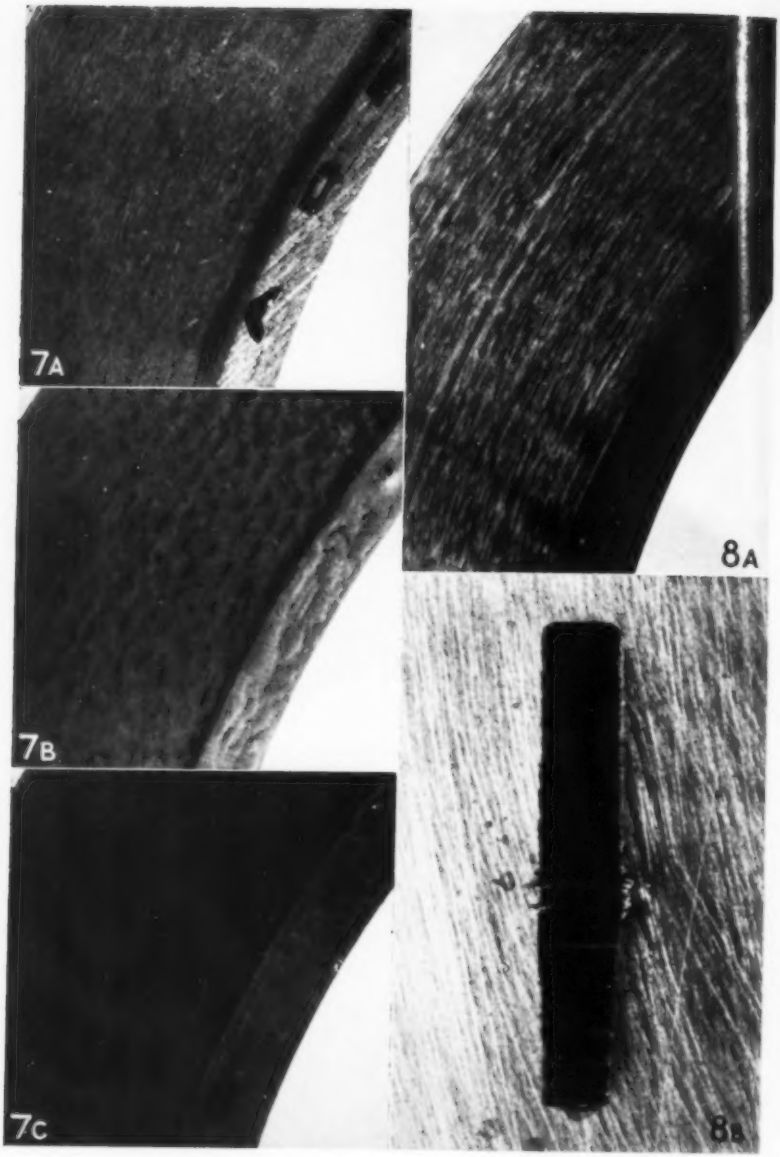

FIG. 7.

(*a*) UNUSED CUP.
(*b*) CUP HEATED FOR 5 MINUTES AT 200° C. IN CHLORINATED DOPE AND WASHED IN OIL AND TRICHLORETHYLENE, SHOWING DELIQUESCENT LAYER.
(*c*) CUP TREATED AS IN (*b*) AND THEN WASHED IN WATER AND DRIED.

FIG. 8 (*a*) AND (*b*).

SMOOTH SCAR OBTAINED WITH UNDOPED OIL UNDER A LOAD OF 70 LB. APPLIED IN THE STANDARD WAY USING A TREATED CUP WHICH HAD NOT BEEN WASHED IN WATER.

higher loads the welding together of the balls may occur. The re-establishment of lubrication does not always take place at a pressure which is completely independent of the load, but it usually varies sufficiently slowly for the mean value to be used as an indication of the intensity of seizure.

Tests with the Rotating Ball Treated before Use.

Tests were carried out with the rotating ball treated in various ways, and the results are given in Table VI.

TABLE VI.

Four-Ball Machine.

Dope Used (expressed as % Cl or % S in doped oil).	State of Top Ball.	2½-Second Seizure Load, kg.	Pressure after Seizure, kg./cm.²
None.	Untreated.	75	500
	Treated in chlorinated dope.	154	500
	Treated in chlorinated dope and washed in water.	137	500
	Treated in HCl.	159	500
	Treated in sulphurized dope.	122	500
3% chlorine.	Untreated.	135	10,000
	Treated in chlorinated dope.	168	13,000
	Treated in chlorinated dope and washed in water.	200	12,000
	Treated in HCl.	258	15,000
	Treated in sulphurized dope.	186	12,000
1% sulphur.	Untreated.	160	3,000
	Treated in chlorinated dope and washed in water.	174	10,000
	Treated in HCl.	190	8,000
	Treated in sulphurized dope.	220	10,000

The oils used with this machine were a mineral oil of viscosity 140 Redwood No. 1 seconds at 200° F., and the same oil containing 3 per cent. of chlorine or 1 per cent. of sulphur in the form of a chlorinated dope and a sulphurized fatty oil, respectively. The reason for using a lower percentage of chlorinated dope on the Timken Machine was merely that the maximum load of that machine was attained rather readily with higher proportions of this material.

The treatment of the balls with both the chlorinated and the sulphurized dopes consisted of heating for 5 minutes at 200° C., followed by cooling the balls in mineral oil and washing them in trichlorethylene. Some of the balls treated with the chlorinated dope were then washed in water and dried; and others were used without further treatment. Washing of the sulphurized balls with benzene, petroleum ether, or water made no difference to the results obtained with undoped oil, and so was not used for the tests with doped oil. The treatment with hydrochloric acid consisted of placing the balls in 10*N*-acid for 5 minutes at 50° C., followed by washing them in water.

It is seen that all the kinds of pretreatment gave rise to marked increases in the 2½-second seizure loads of both doped and undoped oils. Tests with all four balls treated in the same dope gave the same results as were obtained when only the rotating ball had been treated.

Cornell (or Falex) Machine.

The test-pieces used in this machine consist of a piece of ¼-inch steel rod of hardness 5C Rockwell rotating between two V-grooved test-blocks of hardness 10–15C Rockwell. The test-pin is fitted into a chuck which can be rotated at 290 r.p.m., and a piece of thick brass wire placed through holes in the chuck and pin serves to transmit the driving-torque to the pin. The blocks are held against the pin in a pair of jaws by a spring-loading system which is operated by rotation of a ratchet wheel. A device is fitted for rotating the ratchet wheel automatically, and this gives a steadily increasing load, the rate of increase being approximately 1000 lb. per minute. Abrasion of the pin tends to reduce the load on the test-bearing for a given setting of the ratchet wheel, and consequently a constant rate of rotation of the ratchet wheel may not then give a constant rate of increase of load. A hydraulic system is provided to give continuous indication of the friction.

One usual type of test on this machine consists of starting the motor with a small load applied, which is allowed to increase automatically up to 500 lb. The automatic device is then detached to give a running-in period of 5 minutes at this load, after which the load is increased automatically again.

Breakdown of the lubricant is marked by a rapid rise in the frictional torque, and if very severe, by shearing of the brass wire or of the test-pin near the hole through which the wire is fitted.

Abrasion tests in which the load is maintained at a constant value may also be carried out, the abrasion being measured by observing the angle through which the ratchet wheel in the loading device has to be turned in order to maintain the load at a constant value. Tests may also be made in which the load is applied before the motor is started.

All three types of test were carried out with test-pins treated in the chlorinated dope as described for the other two machines, but no significant difference in results was obtained as compared with untreated pins. It was thought that this difference between the Cornell and the other two machines might be due to the relatively low hardness of the test-pieces, and a batch of them were therefore hardened to 60C Rockwell. With these pins the breakdown loads appeared to be beyond the range of the machine, whether the pins were treated or not, and the effects of treatment could therefore not be observed.

Discussion.

Timken Machine.

Treatment of the cups for the Timken machine by (1) running for 10 minutes under a load of 100 lb., whilst lubricated with oil containing the chlorinated dope, (2) heating in the dope, (3) heating in hydrochloric acid,

considerably increased the load withstood when they were subsequently used with undoped oil, whether the load was applied before or after starting the motor. With doped oils an increase could not be observed when the standard method of loading was employed, as the maximum load was withstood by untreated cups; but similar effects were noticed when the motor was started with the load on.

A breakdown load of 20 ± 2 lb. was obtained with undoped oil in a number of ways. Cups treated by running for 10 minutes at 100 lb. in doped oil, or by heating in the dope and washing in water, or by heating in hydrochloric acid and washing in water, all gave this value with either method of loading; and it was also given when testing doped oil with untreated test-pieces by starting the motor with the load on. This agreement may be a coincidence, or it may be connected with the nature of the layers formed by the action of chlorine or hydrochloric acid on a Timken cup.

Four-Ball Machine.

The results obtained with the Four-Ball machine confirmed the increases in breakdown load obtained by treatment on the Timken machine. They also showed that treatment of the top ball does not alter the pressure at which lubrication was re-established by an undoped oil after seizure.

The Temperature Distribution in the Test-pieces.

All the machines described herein have a rotating test-piece in contact with one or more stationary ones. Under the conditions which prevail during the early parts of the tests, the surfaces are separated by a thin layer of oil. The load is carried on local high spots, and the temperatures at the tops of these may reach the melting point of the metal even under comparatively low loads.[6] The temperature of the metal immediately below them will depend on the amount of heat generated at their tops and the rate at which it is conducted away into the body of the test-piece.

The stationary test-pieces are continuously heated during a test, but the rotating ones are cooled by contact with the oil for an appreciable part of each revolution. The metal immediately below the high spots of the stationary test-piece may consequently be expected to be at a higher temperature than the corresponding portions of the rotating ones. It is therefore possible, when a sufficiently high load is used, for this portion of the stationary test-pieces to reach a temperature near the melting point, whilst the corresponding portions of the rotating test-piece are comparatively cool, and welding of metal on to the rotating test-piece can then occur. This occurs when an undoped oil breaks down on each of the three machines described.

When a doped oil is used, the evidence available shows that the coefficient of friction is nearly the same as for an undoped oil in the early part of the test; the presence of the dope cannot therefore affect the temperature distribution appreciably.

Further, loads can be withstood by doped oils which would produce welding with undoped ones. It thus appears that when a dope is used, the metal immediately below the high spots of the stationary test-pieces can be near its melting point without seizure taking place.

The occurrence of such high temperatures in the stationary test-piece without seizure may only lead to an extension of the polishing which occurs at low loads. If the conditions are appropriate, however, it appears that it may lead to appreciable flow of metal from the point of highest temperature in the direction of motion of the test-piece. This is believed to be what takes place when rough scars, such as that shown in Fig. 5, are formed.

Formation of Surface Layers.

The results show that high loads may be withstood by undoped oils without seizure as a result of the previous reaction between the dope and the metal, to form a layer on its surface. This suggests a mechanism for the effects observed with doped oils. These dopes do not react appreciably with metal at ordinary temperatures, and so the layer can only be formed by pretreating the test-pieces, or as a result of the heating they receive during the early part of a test using a doped oil. In the latter case the layer is unlikely to be fully formed before some damage has occurred.

The increased breakdown loads obtained with treated test-pieces may be due to the fact that the full protective layer has been formed in advance. It is therefore possible that improved results might be obtained in practice with doped oils by heating bearing surfaces in the dopes before use. The practice mentioned by Clayton [3, 4] of "running-in" gears with powerful E.P. lubricants and then using them with a milder one is an approximation to this; but even in this case the layer produced by the powerful dope cannot be fully formed without running the risk of damage due to local overheating, and pretreatment with it might give improved results.

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SOME REMARKS REGARDING THE TESTING OF ENGINE LUBRICANTS.*

By C. A. Bouman.†

Synopsis.

Only a few of the characteristics of motor oils can be determined by physical and chemical analysis.

Oxidation tests do not represent the various processes of deterioration taking place in the engine; such great differences exist between processes taking place in various parts of the engine that oils are not rated in the same order of merit for them all. Also, deterioration of engine oil is often a matter of contamination with combustion products, particularly in C.I.-engines.

Carbon tests are only of some value with regard to carbon formation in the combustion space; not, however, with regard to carbon formation in piston-ring grooves or to the tendency to stick rings.

Engine tests are necessary, but wearisome, as the degree of reproducibility required is often too small to allow of reaching a sound conclusion from only a few tests. In particular, the test conditions must also be chosen so as to give a good correlation with those conditions in practice for which an oil is intended.

The reliable judging of lubricating oils is still a source of much worry to the users of oils, to the manufacturers of engines, and to the manufacturers of oils. The most characteristic property of a lubricating oil—viz. its viscosity at various temperatures—can be determined accurately in a very simple way, but there remains the extensive and difficult field of investigation of those properties of an oil which make it either capable or incapable of withstanding the high temperature conditions at various points in the engine. The following remarks mainly concern this field of investigation. Other important properties of engine oils, such as their behaviour at low temperatures, oil consumption, anti-wear characteristics, etc., are left out of account here.

A. Laboratory Oxidation Tests Compared with Practical Results.

For a long time the efforts of many investigators have been directed towards the development of laboratory oxidation tests for lubricating oils. With the aid of these tests it was intended to predict whether a given oil would be suitable for certain types of internal-combustion engines or not. As a result of these attempts, many laboratory oxidation tests, more or less standardized and more or less officially approved, are available or have been suggested. However, it cannot be said that great success has attended these efforts, the main reason being that the deterioration of the oil in the laboratory test and that occurring in internal-combustion engines are of a different nature.

The deterioration processes under high temperature conditions, to which the lubricating oil is exposed in the engine, are of a very complicated character. This applies particularly to those processes which finally result

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in the formation of carbon deposits in the cylinder and on the piston. Further, as is well known, these processes depend very much on engine conditions, especially engine temperatures. When the engine conditions are changed, the intensities of the various processes (oxidation, polymerization, carbonization) to which the lubricating oil is exposed in the engine will also change, and there will be transitions from one process to another. These changes in intensity may be different for various lubricating oils. Testing various oils in one engine under certain test conditions will establish a certain relative rating for the oils. Testing the same oils in another engine or under other engine conditions may establish quite another relative rating.

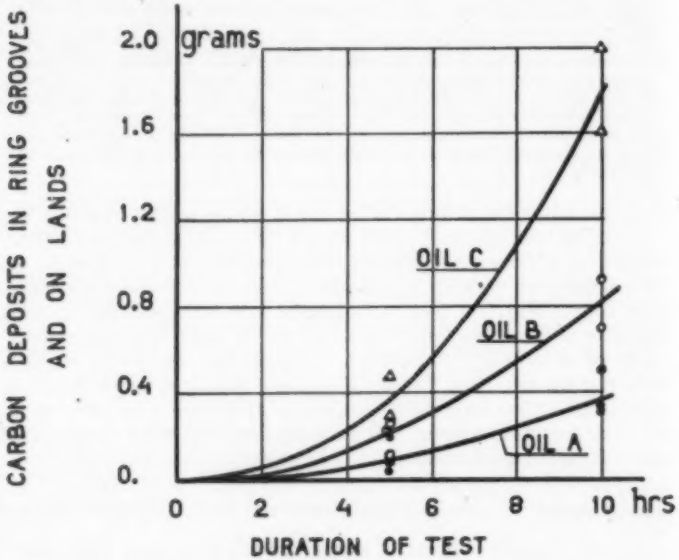

FIG. 1.

CARBON DEPOSITS IN RING GROOVES AND ON LANDS.

Further, it has been confirmed by many results, both in the engine laboratory and in practice, that when testing various oils in a certain engine under certain test conditions, a certain relative rating for the oils as regards the formation of deposits and other undesirable products will be established for one certain spot in the engine; yet in the same engine and under the same test conditions the same oils may show quite another rating for another spot in the engine. Thus, for instance, oils showing a certain relative rating as regards carbon formation in the ring grooves may show quite a different relative rating as regards carbon formation in the combustion space. An example is given in Figs. 1 and 2, showing the results of tests with a single-cylinder horizontal gasoline engine with ethylene glycol cooling, running on three different oils, *A*, *B*, and *C*.

At best the application of the results of laboratory oxidation tests should

be restricted solely to a certain number of the processes taking place in the engine, whereby the temperatures prevailing during a test should be adjusted as closely as possible to the temperature existing or supposed to exist in that part of the engine where the reactions under consideration occur. However, for the study of the more complicated processes occurring in the engine (*e.g.*, ring-sticking) the investigator will necessarily come to a point where he recognizes the desirability of adjusting not only the temperature of his oxidation test to the desired value, but also the mechanical

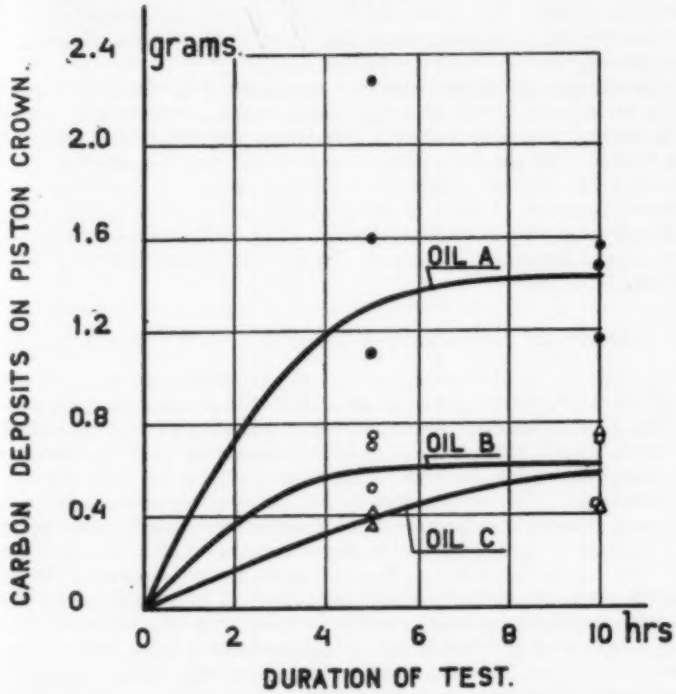

FIG. 2.
CARBON DEPOSITS ON PISTON CROWN.

conditions of the test to those occurring in the engine. This leads to the adoption of so-called semi-technical apparatus.

In many cases the deterioration of the crankcase oil, as measured by the percentage of asphaltenes contained in it, may show a fair correlation with several laboratory tests at moderate temperatures. However, for many engines deterioration of the crankcase oil cannot be measured only by the percentage of asphaltenes contained therein, since in these engines (especially diesel engines) the contamination of the lubricating oil in the crankcase mainly consists of products from incomplete combustion (soot, carbon, lacquer, etc.) of the fuel in the combustion space, which products

have been absorbed by the lubricating oil on the cylinder wall and pass along the piston into the oil in the crankcase. It is quite clear that since an oxidation test only gives data regarding the deterioration of the oil itself, it cannot give any data regarding the contamination of the oil by products formed in the combustion chamber. Therefore, only a very slight value can be attributed to laboratory tests in regard to the judgment of engine-lubricating oils. These tests do not give a correct picture of the manner in which the lubricating oil is contaminated in the engine. At most it must be regarded as a lopsided picture, in which a certain kind of deterioration within the oil is accentuated, therefore giving only an indication in respect of phenomena which, in practice, are found to be relatively unimportant.

It should also be pointed out that the increase in viscosity of the oil during an oxidation test in many cases shows no correlation with its oxidizability. Nor does it show a correlation with practical conditions.

In special cases the laboratory oxidation test can indeed supply useful data regarding the suitability of an oil—*e.g.*, when the crankcase oils of large diesel engines act not only as a lubricant, but also as a cooling medium for the pistons with circulation cooling. The oxidation test then mainly bears on the behaviour of the oil, not as a lubricant, but as a cooling medium.

B. Laboratory Carbonization Tests and Semi-technical Tests.

In addition to the laboratory oxidation tests, which are mainly characterized by the fact that oxygen or air is blown through the oil under certain conditions, other tests have been developed, not so much with the object of measuring the resistance of the oil against deterioration at elevated temperatures, as of measuring the quantity of residue left behind after the oil has been exposed to high temperatures. As examples, the various carbonization tests (Conradson, Ramsbottom) may be mentioned. In the combustion space of an engine the temperatures are so high that it is quite impossible for any lubricating oil to withstand these temperatures without carbonization. Accepting the fact that any oil will carbonize at these temperatures, it nevertheless remains desirable that the oil will leave as small a residue as possible after the carbonization process. To a certain degree the residues found for these tests are a criterion of the volatility of the oil, especially of its heavier components.

Although these carbonization tests may give an indication of the behaviour of the oil when exposed to the combustion temperatures in the combustion space, they cannot give reliable information as regards its tendency to form carbon deposits in other parts of the engine—*e.g.*, in the piston-ring grooves. Moreover, the practical value of the carbonization tests should not be over-estimated, because after a certain quantity of carbon deposit has formed in the combustion space, an equilibrium is obtained : the surface of the carbon deposits has then attained a temperature at which the newly formed carbon particles burn away.

As an intermediate test between oxidation tests and carbonization tests, we may consider the so-called Delft " baking " test, developed by J. E. van Hinte of our Laboratory. With this test about 0·4 gram of the

oil to be investigated is submitted to various constant temperatures (270–290° C.) for a certain time (about 40 minutes) in a small open aluminium cup. At the end of the test the loss by evaporation and the residue (insoluble in non-aromatic gasoline 60/80) are measured.

Another test on the same lines is the Wright Aeronautical Corporation's oxidation cup test.[1] The Delft "baking" test is now being modified by placing small steel discs on the oil layer at the bottom of the cup, so that it is now a combined baking and sticking test. In a few cases satisfactory correlation was found between the results of the baking test and the results of ring-sticking tests in the engine.

Further development of semi-technical testing equipment would be directed towards realizing in the apparatus as closely as possible the physical and mechanical conditions prevailing in an engine. It will be found in the long run, however, that tests on actual gasoline or diesel engines are not only simpler, but also far more reliable than tests with such apparatus.

C. Engine Tests.

In most cases, especially when the tendency of the oil to cause ring-sticking is to be studied, testing in the engine is the only way to obtain reliable information regarding the quality of the oil. Unfortunately, the engine tests also present considerable difficulties, mainly for two reasons. In the first place, when preliminary testing of aviation oils and of marine diesel-engine oils is conducted in relatively small gasoline and diesel engines, the question arises whether the results obtained with such small engines are applicable to the actual engines in practice. Secondly, the reproducibility of engine-fouling tests is often unsatisfactory, which fact, of course, tends to make the results confusing.

As to the first point, it has been found that when marine diesel-engine oils are tested in small diesel engines, and when aviation oils are tested in small gasoline engines, the classification of various lubricating oils as determined in the small oil-testing engines generally agrees to a satisfactory extent with the classification of the same oils in practice.[2]

In order to shorten the duration of the tests, the engine conditions may be made somewhat more severe than those occurring in practice. It has been found that when these changes are kept within reasonable limits, the relative classification of the oils is not affected too much.

The most difficult and at the same time most important point in the engine-testing of lubricating oils is the degree of *reproducibility* which can be obtained when tests are repeated under conditions as nearly identical as possible. A few remarks concerning this problem may be given with regard to determining the tendency to ring-sticking and carbon formation on the piston. First of all, it is important to note that an agglomeration of fouling products from the oil (together with contamination products from combustion) formed during a relatively long running time constitutes the tangible result of a test. In this respect there is a marked difference between the testing of lubricating oils and, for instance, the testing of the ignition quality of diesel fuels. In the latter case the result of the test is, in principle, obtained during only one cycle of the process, in the course of which the product (fuel) to be investigated is consumed. A new charge is

supplied for the next cycle. Thus, no disturbing influences from previous cycles on the results are encountered. On the contrary, the accuracy can be improved by taking the average results of a great many cycles.

When combustion phenomena are studied, such as the tendency of fuels containing residual components to form carbon deposits on some spot of the combustion space, the results are an agglomeration of products formed over a long period, and it is known that the reproducibility of tests of that kind

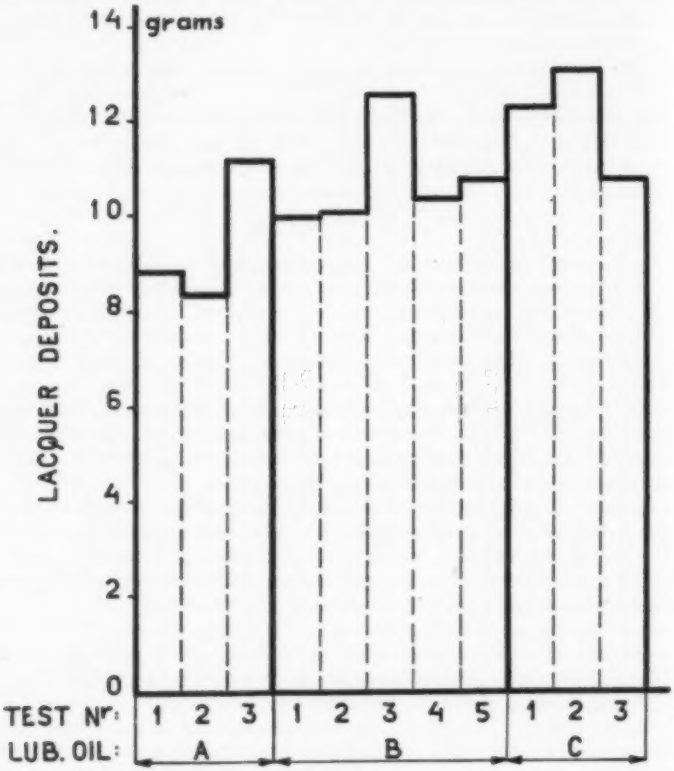

FIG. 3.

FAIR REPRODUCIBILITY OF LACQUER TESTS WITH AIR-INJECTION DIESEL ENGINE AT LOW LOAD.

is smaller than that of ignition quality measurements. Such unfavourable circumstances are always met with during tests with engine-lubricating oils. As regards ring-sticking tests, there is a further reason for the lack of reproducibility—viz., the fact that the ring-sticking phenomenon depends to a very great extent on the mechanical conditions of the piston and piston-rings. As such may be mentioned the side clearances of the piston-rings in their grooves, the elasticity (radial pressure) of the rings, the initiation

of ring-sticking by adventitious accumulation of ring-blocking material somewhere along the ring circumference, the circumstance whether ring-sticking starts at the gap or at another point of the ring circumference, the degree to which heat-flow and blow-by are affected by initial ring-sticking, the thermal distortion of piston and cylinder, oil consumption, etc. All these factors cannot be kept under absolute control during a test. Also difficulties may arise as to the interpretation of the results, when, for

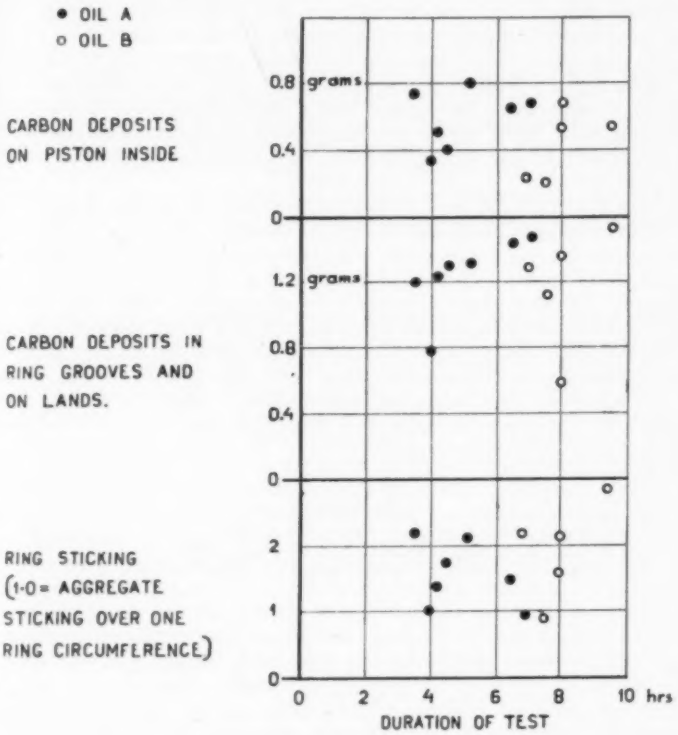

FIG. 4.

CASE OF POOR REPRODUCIBILITY OF RING-STICKING TESTS ON DIESEL ENGINE WITH ETHYLENE GLYCOL COOLING.

instance, only the gap of the ring is stuck (both ends), whilst the other parts of the circumference are still free, and further, when a ring is still "just free" or is only "slightly sticking," etc.

Examples covering the degrees of reproducibility of engine-fouling tests are given in Figs. 3 and 4. Fig. 3 represents the amount of lacquer deposit scraped off from the piston and liner surface of a 50-h.p. air-injection diesel engine for a number of nine-hour tests at 15 per cent. load and 44-atm. air-injection pressure. Various tests were carried out with three different

lubricating oils; each horizontal part of the stepped line represents the result of a single test. The reproducibility of these tests is very reasonable, and the average differences between the three lubricating oils A, B, and C are only small. This result tallies with the fact that the lacquer deposits referred to are due to incomplete combustion of the fuel.

Another example is shown in Fig. 4, where the results are given of ring-sticking tests with a small pre-combustion chamber diesel engine, running under high-temperature conditions (ethylene glycol cooling). The reproducibility of these tests was rather poor, but seeing that relatively many tests were carried out on each oil, a conclusion can be reached—viz., that oil B is superior to oil A, since, on the average, it allows the engine to run longer for a given amount of ring-sticking. Under such circumstances the only way seems to be to conduct many experiments, in order to obtain statistical data, which enable a conclusion to be drawn. Fortunately the reproducibility of ring-sticking tests is often much better than in the case of Fig. 4.

As the test results depend to such a great extent on mechanical conditions of the engine, engine lubricating-oil tests should, in general, be of a comparative nature. Thus, the behaviour of an oil to be investigated should be compared with that of another oil which has been adopted as a standard. In most cases it is precisely comparative tests with different oils that are wanted, especially when the effect of dopes has to be studied.

Although the testing of lubricating oils in engines is difficult and costs a great deal of time, it has nevertheless to be done in view of the necessity of developing oils with improved characteristics, especially as regards the tendency to cause ring-sticking, and the utter impossibility of achieving the results by any other means.

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[1] Beall, A. L., *J. Soc. aut. Engrs*, Feb., 1937.
[2] Bass, E. L., and Barton, C. H., *ibid.*, Jan., 1939.
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PISTON AND PISTON-RING TEMPERATURES *

By P. V. Keyser,† Jr., and E. F. Miller.†

Synopsis.

Piston deposits—Methods of measuring piston temperature—Cylinder wall temperature measurement—Laboratory experiments—Effect of design on piston temperature.

Introduction.

The increase in the specific output of internal-combustion engines in recent years has brought about a number of lubrication problems. Figuring prominently among these is the problem of piston lubrication, which has resulted from the excessive piston temperatures occurring in the piston-ring zone, particularly in high-speed automotive diesel engines. Many of the lubrication practices which are entirely satisfactory in large slow-speed diesel engines are not applicable to the present high-speed types.

Piston Deposits.

The problem of developing an oil which will permit engine operation at piston temperatures of the order of 450° F. in the ring zone is a problem of limiting the extent and nature of carbon formation. The importance of piston temperature might be summed up generally by stating that piston deposits are for the most part the result of some temperature condition existing at the point of deposit. Fig. 8 is presented to indicate the types of deposit likely to be found at various points of a diesel piston together with the approximate corresponding temperatures. On the top land of the piston it is usual to find a rather hard deposit of carbon, which will be formed in a region of temperature of about 550° F. This deposit is sometimes abrasive, and may lead to various degrees of scuffing of the piston and cylinder wall, depending on the load conditions. The deposit found in the piston-ring grooves is a rather dry carbon ranging from soft to hard, depending on the type of oil used. This deposit will be heaviest in the top ring groove, decreasing amounts being found as the oil-ring groove is approached. The temperature range from the top to the third-ring groove is usually from about 450° F. to 350° F. The accumulation of carbon behind the top piston ring can cause abnormally high ring-wall pressures leading to scuffing of the piston ring and cylinder wall. Sludge is invariably deposited in the oil-ring groove in amounts varying with the degree of instability of the lubricating oil and the incompleteness of combustion. The upper part of the piston skirt usually exhibits a varnish-like deposit, the tenacity of which is a function of the type of oil used. This deposit is heaviest on the skirt areas closest to the piston pin, where the pressure of the piston against the cylinder is not sufficient to keep the surface wiped clean. A similar but lighter varnish frequently forms on

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the piston-pin bearings. In the piston-pin relief areas and also on other parts of the skirt an oily soot is often encountered. It is believed that this deposit consists mainly of products of incomplete combustion of fuel and lubricating oil that are scraped down the cylinder wall by the piston rings. It is this sooty formation which, on reaching the crankcase, causes the blackening of the lubricating oil. This is a characteristic which is typical of some high-speed diesel engines.

The designer of a piston is faced with the problem of temperature control. If he chooses to use aluminum instead of iron or steel, in order to make use of the greater heat conductivity of aluminum, he must provide sufficient clearance between the piston and cylinder wall when the engine is cold to forestall the possibility of piston seizure when the engine is run under heavy load. There is the problem of providing sufficient strength when the piston operates at high temperature and pressure due to heavy load. The designer must consider the possibility of localized heating, which can cause piston distortion, and, if great enough, can cause piston fracture because of unequal expansion. Generally, then, it might be said that the maximum continuous operating load of an engine is limited largely by the maximum piston temperature which will allow satisfactory lubrication. Since supercharging provides an effective method of increasing the output of an engine, it appears that it can be done only if a satisfactory means is employed for limiting the maximum piston temperature.

Methods of Measuring Piston Temperature.

In the course of the lubricating-oil development work at the Socony-Vacuum Oil Company's laboratories, it has been found useful to make a study of piston temperatures. Most of the work has centred about the temperature studies in connection with the lubrication of diesel engines. A short investigation has also been made of the temperatures occurring in a small single-cylinder gasoline engine.

There are several methods which can be used for measuring piston temperature. One system that is sometimes used is that of the continuous-contact type, in which a thermocouple is embedded in the piston at the desired point and led by a flexible wire, made up of iron and constantan, along suitable supports to a point outside the engine. This system, although giving reliable results, can hardly be used on engines which operate at speeds approaching 2000 r.p.m. Another method of piston-temperature measurement is one in which fusible plugs are used. Alloys of known melting points are securely placed in holes drilled in the piston. The engine is then run at the desired set of conditions until the operating temperatures become stabilized, whereupon the engine is shut down and the piston inspected. By noting which of the alloys have melted, one can determine the piston temperature. This method presents the serious disadvantage that only one set of temperatures can be determined at one time, after which the engine must be taken apart and inspected

A third system, and the one which was used in most of our tests, is the intermittent contact thermocouple type. This method was suggested to us by the General Motors Corporation. A diagrammatic sketch of the system is presented in Fig. 1. The thermocouple in the piston is connected to

contacts at the bottom of the piston. These contacts mate with spring-loaded contacts attached to a bracket on the liner. The contacts in each case are made of the same metal as is the leg of the thermocouple it con-

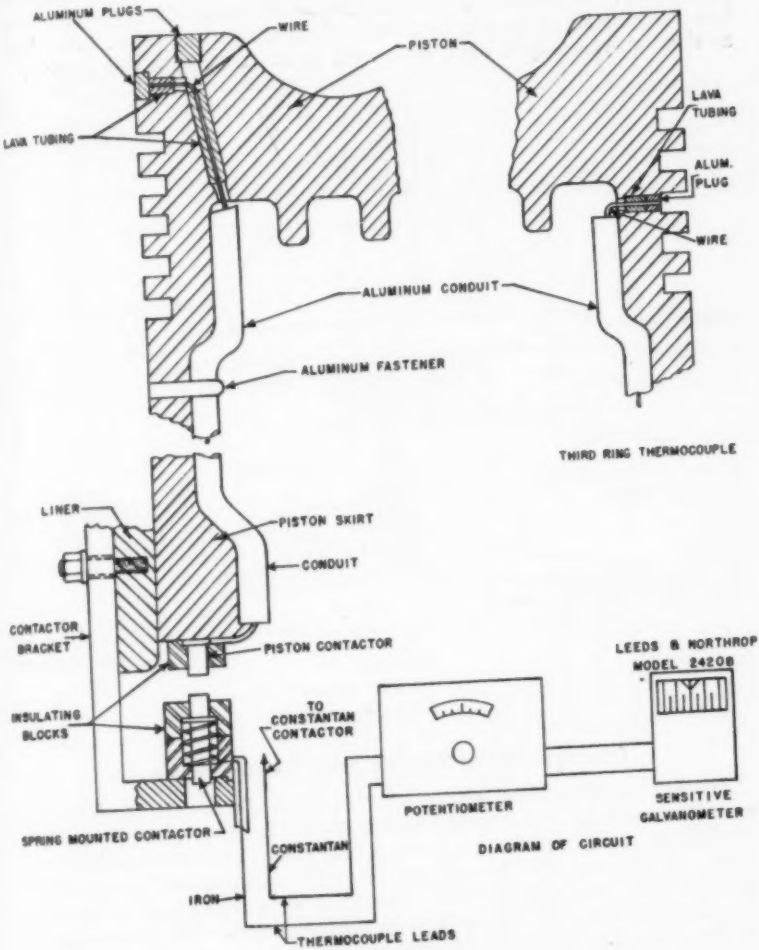


FIG. 1.

nects. The springs loading the movable contacts are of spring steel, and as there is little or no temperature drop across the spring, it is believed that no error is incurred through the insertion of the third metal. It will be noted from the drawing that lava tubing insulates the wire in the holes drilled in the piston. The wires emerging from the lava tubing are then

wrapped with mica tape and inserted in aluminum conduit. The conduit is attached to the piston in several places to prevent vibration. The wires are soldered to the contacts on the piston. Likewise, the wires connecting the potentiometer to the movable contacts are soldered to the springs. A duration of contact of 35° of crankshaft angle has been found to give ample sensitivity with the instruments employed. As many as three thermocouples have been used at one time with this system.

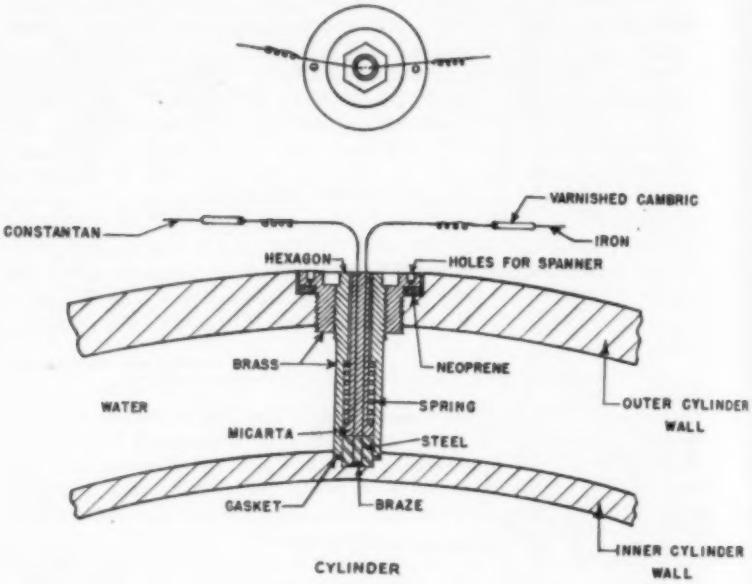


FIG. 2.

CYLINDER-WALL TEMPERATURE MEASUREMENT.

Another useful tool in the laboratory is a method of measuring cylinder-wall temperature. Such measurements give a reliable indication of the lubrication conditions existing between the piston and cylinder-wall surfaces. A thermocouple placed near the inner cylinder wall provides an effective method of making such measurements. Several types of thermocouple installations have been tried in our laboratory. The design shown in Fig. 2 has given excellent performance, responding rapidly to changes in engine operating conditions. Care must be exercised in the installation of the thermocouple to prevent cylinder-wall distortion. Several distances of the thermocouple from the inner wall were tried, including the embodying of the thermocouple flush with the inner wall. It was found that a distance of 0·040 in. from the inner wall gave, as far as we could determine, a thermocouple that was just as sensitive as the one which was flush with the inner

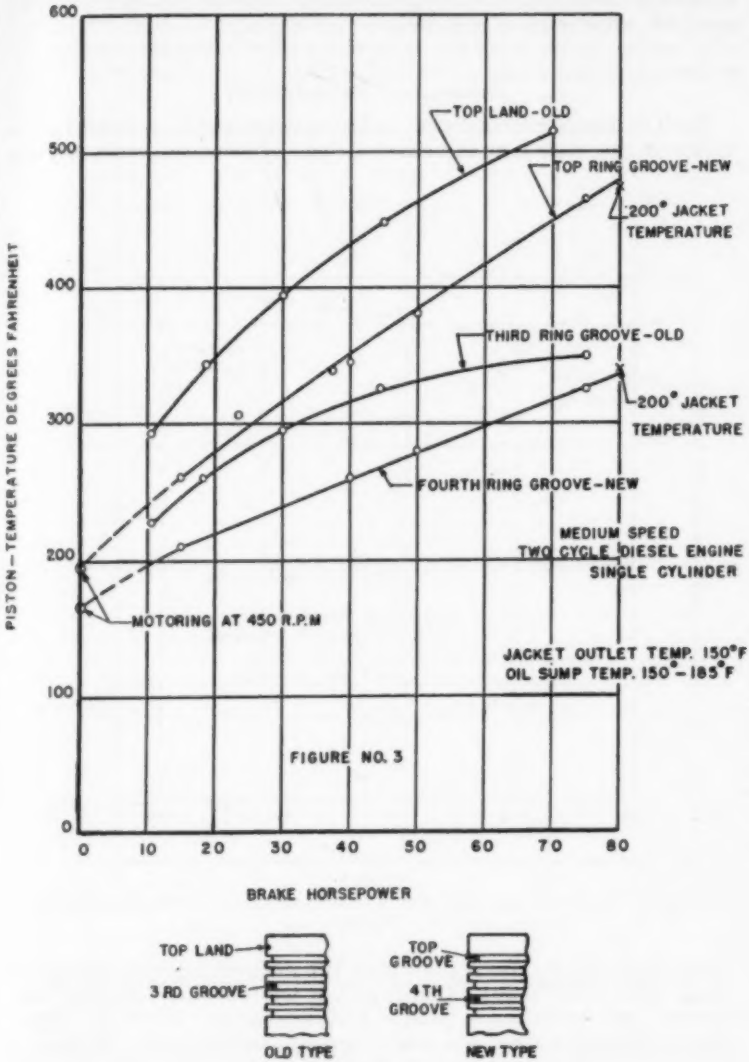


FIG. 3.

EFFECT OF LOAD ON PISTON TEMPERATURE.

wall. This thermocouple was used in an engine equipped with a cylinder liner of the wet type. The design, however, could be modified to permit use with other types of cylinders.

Laboratory Experiments.

Much of the experimental work on piston temperature has centred about measurements made in an experimental single-cylinder, two-cycle, medium-

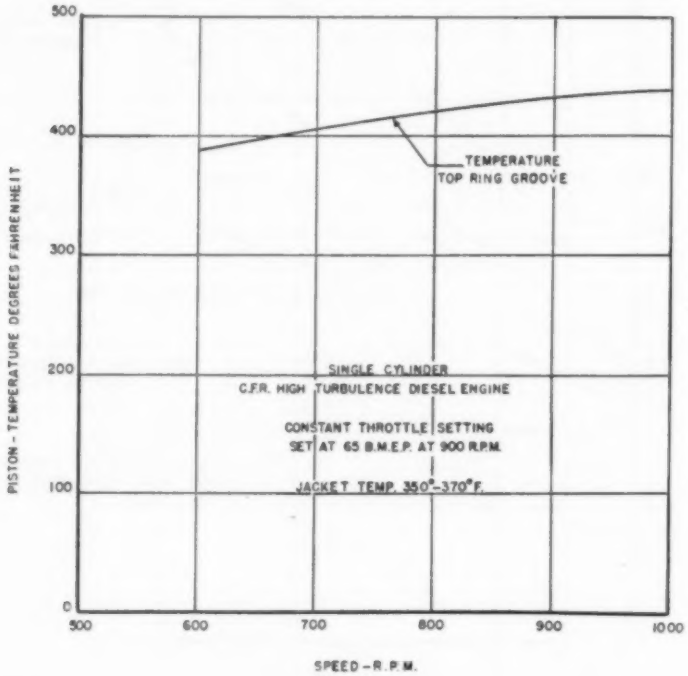


Fig. 4.

EFFECT OF ENGINE SPEED UPON PISTON TEMPERATURE AT CONSTANT THROTTLE SETTING.

speed diesel engine. During this work two different types of pistons were used. The piston called "Old Type" in the following discussion has a waffled inner crown and is made of aluminum alloy. The "New Type," also of aluminum alloy, has many deep ribs on the piston interior. In both cases oil is sprayed from the top of the connecting-rod on the under side of the head of the piston. The New Type piston is fitted with a metal baffle which traps oil in the interior of the piston for the purpose of cooling.

The intermittent-contact type of thermocouple described above was used in the piston-temperature measurements made in this engine. The results

are summarized in the form of curves presented in Fig. 3. These curves show the effect of horse-power output on piston-ring groove temperature. Both speed and throttle position were varied in these tests, the lower horse-powers naturally being obtained at the lower engine speeds. The curves show that any oil which reaches the top piston-ring groove will be

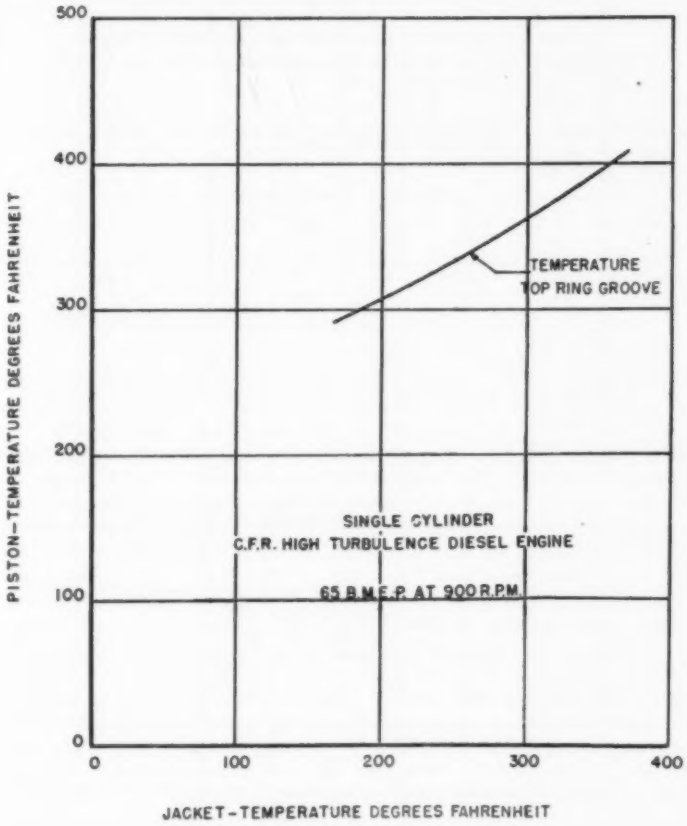


FIG. 5.

EFFECT OF COOLING JACKET TEMPERATURE UPON PISTON TEMPERATURE AT CONSTANT LOAD.

subjected to a temperature of 440° F. (227° C.) when the engine is operated at 75 h.p. The effect of speed on piston temperature at constant horse-power output is shown in Table I. It appears that when the engine was operated at constant horse-power at low outputs, there was a small increase in piston temperature with speed. When the engine was operated at 40 h.p. there was practically no change in temperature with speed.

Piston-temperature measurements were made on a Co-operative Fuel Research High-turbulence Single-Cylinder Diesel Engine by the intermittent contact method. The engine was fitted with an aluminum piston for this work. Two curves are presented, Fig. 4 showing the effect of load

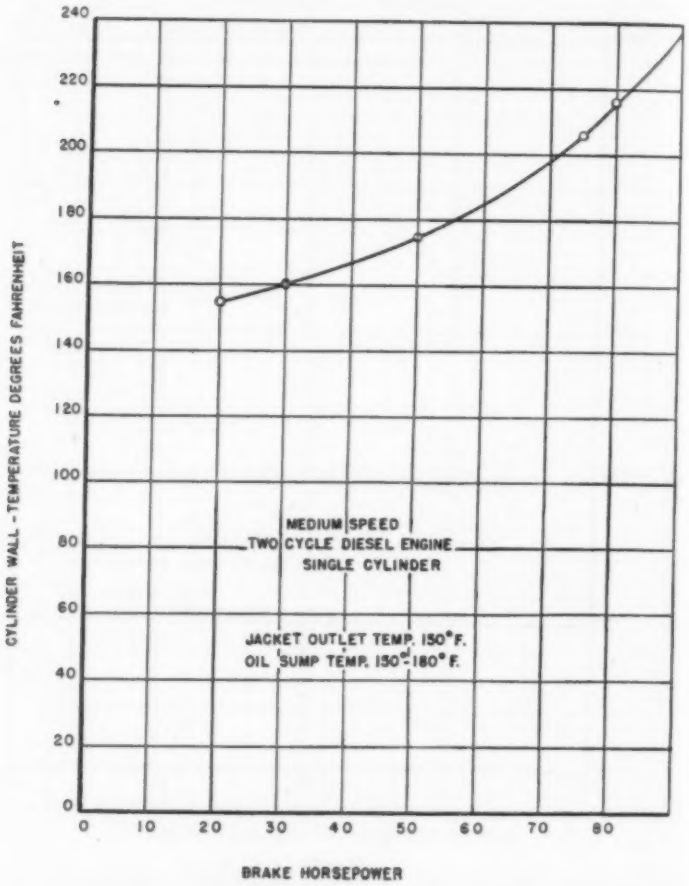


FIG. 6.

EFFECT OF LOAD ON CYLINDER-WALL TEMPERATURE.

on piston temperature at constant throttle setting, and Fig. 5 showing the effect of jacket temperature on piston temperature. In both tests ethylene glycol was the jacket coolant. From Fig. 5 it appears that a decrease of 100° F. in jacket temperature will bring about a reduction in piston temperature of about 50° F.

The effect of horse-power output on cylinder-wall temperature was investigated in the medium-speed two-cycle engine. These results are plotted in Fig. 6. In this test both speed and load were varied keeping the water outlet temperature constant at 150° F. The changes in cylinder-wall temperature, therefore, are the result of changes in both load and piston speed.

TABLE I.

Effect of Speed on Piston Temperature at Constant B.H.P.

r.p.m.	Beam Load, lb.	b.h.p.	Temperature Degrees Fahrenheit				
			Jacket	Oil	Cylinder wall	Top ring groove	Fourth ring groove
433	102	14·7	148	130	160	250	205
752	60	15·1	150	165	165	295	230
580	152	29·4	150	155	160	305	225
746	119	29·6	151	160	170	330	245
594	202	40·0	150	157	170	345	255
754	159	40·0	150	170	170	345	260

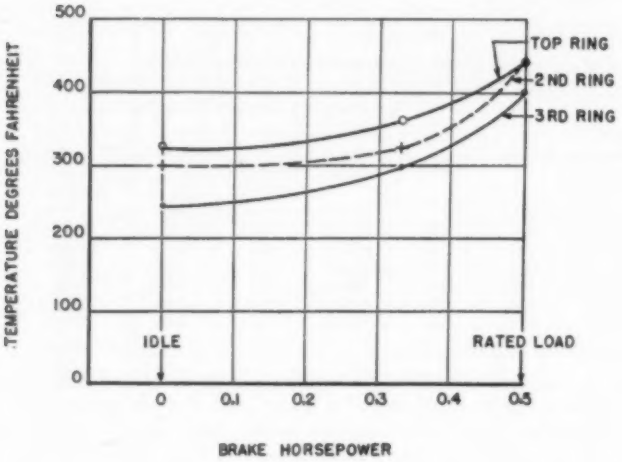
It was found on several occasions that when a new liner and piston assembly were installed in the engine and a heavy load was placed on the engine before the piston rings were properly seated, that blowby would result. Under these conditions the blowby gave an immediate rise in cylinder-wall temperature as indicated by the cylinder-wall thermocouple. The same condition resulted when blowby caused by ring sticking occurred. The cylinder-wall thermocouple connected to a temperature recorder provides a useful tool, especially on this a two-cycle engine where a quantitative measure of blowby is impossible because of the ports in the cylinder liner.

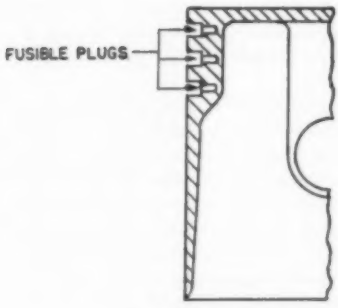
Piston-temperature measurements have been made in a single-cylinder, four-cycle, air-cooled gasoline engine, having a $2\frac{1}{2}$-in. bore and $1\frac{3}{4}$-in. stroke. The fins on the air-cooled cylinder are spaced to about a $\frac{1}{2}$-in. pitch. Fig. 7 shows the variation of piston temperature with load at constant speed as determined by the fusible-plug method. These tests indicate that in this engine the second piston-ring groove operates at a temperature approximating to that of the top ring groove. It will be noted that the temperature of the top piston-ring groove in the air-cooled engine is about 440° F. (227° C.), or about the same as the temperature of the top ring groove in the medium-speed two-cycle engine. A rough indication can be obtained from this comparison of the price which must be paid for such air-cooling of engines, for here we observe that although the air-cooled engine is operating at an output of only 36 lb./sq. in. B.M.E.P., the piston temperature is just as high as in the water-cooled, two-cycle engine when operated at a B.M.E.P. of about 80 lb. per square inch.

EFFECT OF DESIGN ON PISTON TEMPERATURE.

The heat in the piston-ring zone is dissipated in several ways. A considerable amount is conducted away from the piston through the piston

rings which are pressing against the relatively cool cylinder wall. Some heat will be taken up by the lubricating oil which comes in contact with the inner crown of the piston. Heat is conducted to the piston skirt, which in turn transmits the heat to the cylinder wall. A small portion of the





SINGLE CYLINDER
AIR COOLED GASOLINE ENGINE
FOUR CYCLE
BORE-2 1/8 IN. STROKE-1 3/4 IN.
RATED LOAD-1/2 H.P. AT 1800 R.P.M.
B.M.E.P. AT RATED LOAD-36 LBS. PER SQ. IN.

FIG. 7.

EFFECT OF LOAD ON PISTON TEMPERATURE AT CONSTANT SPEED.

heat is carried through the wrist-pin to the connecting-rod, and then dissipated to the crankshaft. The amount of heat thus conducted has been known, in unusual cases, to cause the bearing temperature to be sufficiently high as to necessitate a change in design. A heat groove above the top piston-ring groove is sometimes employed in an endeavour to

prevent the heat from the head of the piston from being transferred to the immediate vicinity of the top-ring groove. Instead the heat tends to be distributed more uniformly over all the piston-ring grooves. Too much dependence cannot be placed on this method of controlling piston temperature, for the effectiveness of the heat groove is probably reduced with service because of carbonization. A method of limiting the amount of heat reaching the piston-ring zone is that in which the path of the heat from the head of the piston is restricted by making the piston material above the top piston-ring groove very thin, and to use oil sprayed from the top of the connecting-rod for cooling purposes. Pistons of this type are usually made of iron or steel, for it is desired to restrict the flow of

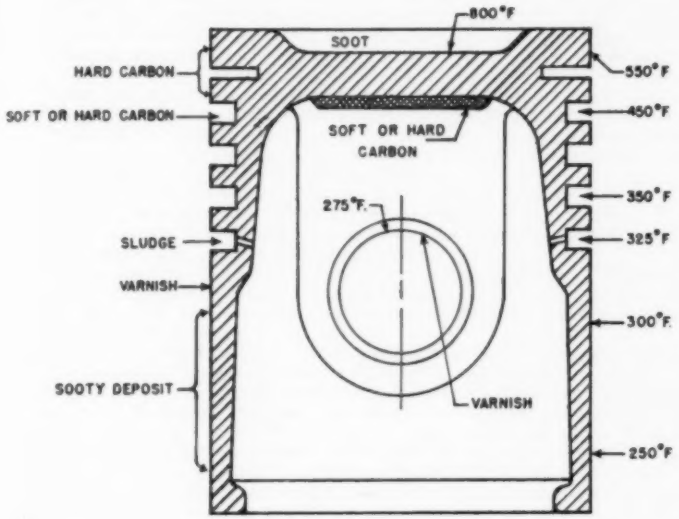


FIG. 8.

NATURE OF PISTON DEPOSITS AND CORRESPONDING PISTON TEMPERATURES.

heat as much as possible. Also, it is necessary to use a strong material because of the thinness of the section connecting the piston-ring region with the piston head. In engines employing an ante-chamber to control the combustion process, the practice of directing the throat of the ante-chamber toward the piston causes localized heating, sometimes sufficient to cause ring-sticking at the latter point.

It must not be inferred from the above discussion that it is desired to have the piston run as cool as possible, for, assuming that the temperature of the piston could be reduced to some very low figure—say 150° F.—to do so would handicap the combustion process by increasing the delay period and promoting incomplete combustion. In this connectiom it should be mentioned that pistons are sometimes cupped at the top so as to form a large percentage of the area of the combustion chamber. This is done

to assist combustion of the fuel, the hot surface of the piston taking the place of the comparatively cool cylinder wall. At first thought one might think that the designer of a piston must choose a temperature at which he desires the piston to operate, and then design the piston accordingly. This is hardly the case, however, for the designer will have all he can do to bring the piston temperature down to a point where an engine may be operated at high output without resulting in severe punishment of the lubricating oil.

Morning Session B, Wednesday, May 24th.

Papers on Testing of Lubricants.

REPORTER'S SUMMARY OF PAPERS.

(Mr. E. A. Evans, M.A.I.E., F.Inst.Pet.)

Mr. E. A. Evans, in summarizing the Papers on Testing of Lubricants presented at the Morning Session on May 24th, said that lopsidedness was not a word which came easily to the mouth of an Englishman, but Bouman used it in his papers with emphasis. It was descriptive, and produced a picture of errors which the Institute of Petroleum was anxious to eliminate. A lopsided conception of lubrication was fatal to progressive thought. In the past much time had been devoted to chemical and physical testing of lubricants, and still the struggle went on; they were ever hopeful of achieving a useful result. Throughout that struggle there had been a consciousness that mechanical testing might be introduced to short-circuit the would-be academic attack. Many years ago Thurston designed a friction testing machine to study oiliness. Improvements and modifications had appeared and faded away, leaving behind much the same speculation as that which had preceded them. Relatively slow speeds and low pressures did not present a real lubrication difficulty, but when speeds began to increase, engine power shot up, and the whole train of engineering progress became alarmingly dependent on lubricants and lubrication.

New methods for development were necessary. It was no longer safe to take a chance, fortified only with some physical measurement such as viscosity. It certainly was not economic to await the laborious findings of a full-scale engine or machine test. Dimensional or mechanical testing became imperative.

At that time mechanical testing of lubricants was standard practice. The objective of the papers in this section was to survey mechanical testing with a view to standardization, and so to eliminate any lopsidedness which might exist in appraising lubricants for specific purposes.

Bouman had waged a minor war, in the past, on the supposed value of oxidation tests as the criteria of oil decomposition in an engine. He had returned to the fray with more ammunition to defend his front. Nobody would disagree with him in his suggestion that the changes which occurred within the oil in an internal-combustion engine were very complicated; likewise there would be agreement on his remark that there was a variety of conditions in the engine which would produce a variation of reactions. It was too much to hope that one could reproduce all those conditions on a laboratory bench. It was much simpler and more reliable to resort to mechanical testing in an engine. Bouman had shown that, with the aid of an engine, it was possible to give a quality rating for oil. The three oils which he used were placed in their respective positions according to the amount of carbon in the ring grooves, but when they were rated according to the weight of carbon on the piston crown, the order was reversed.

Bouman was not so bold as to condemn an oxidation test. He admitted that it had a limited sphere of usefulness, and referred to the so-called Delft "baking" test, developed in his own laboratory. This test seemed to be almost identical with that described to the Institute by Hoblyn in 1925. Bouman was not the man to introduce an air of finality into his paper; on the contrary, he had reopened an old controversy. He was alive to all the difficulties encountered in engine testing, but however great they might be, they must not eclipse the desire to introduce engine testing into a research problem. He cited results, obtained when using a compression-ignition engine, which went to show that the study of the lubricating oil was insufficient without due regard to the fuel influence. None of those results could be obtained by any other means than engine testing.

The paper by McNicol, Williams, and Lamarque formed a pleasant link with Bouman's. They did not propose a new test, but modestly described an experimental technique extremely simple in character, but full of possibility. The extensive facilities which they possessed at the Research Laboratory of the Institution of Automobile Engineers led one to postulate that engine tests would be made, to prove or

disprove the practical value of the test for the ring-sticking properties of lubricants. Before leaving the subject, it would be interesting to know whether ring-sticking was a common phenomenon with low-viscosity solvent oils.

So much uncertainty existed about the evaluation of extreme pressure lubricants that another opportunity to consider the subject was welcomed. There was no universally accepted test machine. It was probable that standardization could not be effected until much more was known about film rupture strength and the influence of surface finish.

Clayton's paper at the General Discussion on Lubrication arranged by the Institution of Mechanical Engineers in 1937 did not create the interest which it warranted, possibly because the Four Ball Machine was not widely known except by name. To follow his present paper it might be necessary to be reminded that three ½-in. steel balls were placed in a small oil-bath, and a fourth ball was superimposed so that it was in contact with the other three balls. The top ball was rotated at 1500 r.p.m. The great feature of the machine was that four balls were in point contact, and as soon as a load was applied, boundary conditions existed. When a load was applied there was obviously some slight deformation of the balls, so, instead of having point contact, there was a slight depression, which could be calculated according to the Hertz theory. Any depression larger than that must be due to wear. At a certain load the oil film broke down and the balls seized. The seizure might be so drastic that the balls welded together. On the other hand, the seizure might be slight, and only noticed by a sudden rise in friction. At the moment of seizure rapid wear occurred, the impression was increased in size, and the friction diminished. The lubricant had, in fact, effected a recovery.

In making a test all that one had to do was to put a load on to the lever and run for one minute after connecting the oil-bath to a revolving drum which measured friction or torque. At the end of the run the diameter of the impression was measured and plotted against load. From a series of runs a graph could be drawn. When a seizure occurred, a rapid increase in the size of the impression resulted, which was depicted in Fig. 2. The significance of that was merely that it indicated the load at which breakdown took place, quite irrespective of time. The time to seizure against load was of importance only if it could be correlated with practice. It had been found that the load which caused seizure in 2½ secs. gave an indication of the suitability of the lubricant for a hypoid gear. The friction-time chart showed the recovery time. An oil which seized but recovered quickly was better than one which had a long recovery time. An oil which did not seize was the ideal, provided it did not possess the other features which condemned it.

Oil *E*, containing 10 per cent. lead soap and 2¼ per cent. sulphur, gave no breakdown as shown in Fig. 4*b*. Oil *G*, containing 4½ per cent. lead soap, gave similar results to oil *E*, except that at 150 kg. wear rose to almost double that of oil *E*. The increase in wear appeared to be due to the smaller content of lead soap. Oil *F*, containing 13½ per cent. fatty oil, 1½ per cent. sulphur, and 10 per cent. chlorinated product (3 per cent. chlorine) was described by the makers as "mild," yet behaved as oil *E*, and better than oil *G*. Evidently the improvement was due to the chlorinated product.

Finally, Clayton gave the results of tests on several mineral oils, and came to the conclusion that solvent refined oils were inferior to conventionally refined oils in film rupture strength. That suggestion was too sweeping, because it was not confined to one solvent or one type of oil, nor to any particular degree of refining.

Assuming that a hypoid gear acquired a "surface" during its early life in an E.P. lubricant, Baxter, Snow, and Pierce studied the pre-treatment of the test-pieces in E.P. test machines. Their paper gave sufficient data to prove that pre-treatment gave rise to marked increases in load-carrying capacity to both doped and undoped oils. That was most important, therefore the paper should commend itself to motor-car manufacturers.

The term "dope" was so loosely used at that time that it might very well give rise to a wrong impression. Surely it was preferable to refer to an E.P. addition agent.

So far consideration had only been given to E.P. oils. Evans introduced E.P. greases. Admittedly at the present time they were mainly used in large roller bearings, but when they once became established their use would obviously be extended. They differed from oils in that an E.P. addition agent was insufficient to produce E.P. properties. As Evans was one of the very few people who had given serious consideration to E.P. greases, his paper should be studied in its entirety.

Grease had been improved in recent years mainly under the compulsion of the anti-friction-bearing makers. It was a mistake to think that one grease was suitable for all makes of ball or roller bearings. Evans made a very strong plea in favour of certain lime-soap greases. He was not ready to accept any type of lime-soap grease. In fact, he had laid down a very rigid specification. It was probable that it was very largely through his efforts that grease-makers had improved the stability of greases. Grease-makers might not like to acknowledge that they had received an ultimatum, but it must be acknowledged that the Timken stability test had become both popular and important. The arguments of Evans in favour of the lime-soap greases were clearly set out in that paper. He stated that it might not be common knowledge that although the melting point of the soda grease was higher than that of the lime-soap grease, the consistency of each at temperatures of 140° F. and above was approximately the same, making allowances, of course, for the consistency at atmospheric temperature. The relative merits of lime and soda-soap greases for anti-friction bearings made a very controversial subject. Perhaps, however, the subject was not quite so controversial as it might appear at first sight. Evans told us that he preferred a medium viscosity oil in the grease for the Timken bearing. The Hoffmann Manufacturing Company generally preferred a lower viscosity oil. That difference of opinion was not based on some theoretical consideration, but was actually due to the difference in the design of the bearings. Perhaps the discussion might reveal points of view which might help to clarify some of those apparent anomalies. If there should not be an opportunity for clarifying them at the meeting, there would be facilities for further discussion at the Lubrication Group Meeting which had been arranged to take place in October.

The Timken machine was used by Evans for measuring the extreme pressure characteristics of both oils and greases. That machine appeared to have suffered the same fate as many other allied machines in the U.S.A. Whether some of those machines would be restored to favour, however, now that the mild E.P. lubricant was being reinstated, it was difficult to tell. For E.P. greases, however, the Timken machine did not appear to have a serious rival. It was interesting to note that when using that machine there was some support for the suggestion made by Baxter, Snow, and Pierce, that oils containing chlorine compounds show less wear than those which contain sulphur. Another very interesting point which was emphasized was the effect of finish on film strength. The importance of that could not be overstated, but whether it was cheaper to produce an ideal finish in the engineering shop, or in the back axle with the aid of an E.P. lubricant, must be left to experts in costing. The scientific mind of the engineer would no doubt prefer the result of his own art, whereas that of the chemist might favour the physico-chemical reactions between active compounds in the lubricant and the metal surfaces.

Were they really safe in coming to definite conclusions about the properties of chlorine when only one or two chlorine compounds had been tried?

If they accepted the authors' views, it appeared that they had learned that :—

(1) Mechanical testing was essential;
(2) Oxidation tests were misleading;
(3) Chlorine compounds were serious competitors to sulphur compounds;
(4) Pre-treatment of gears was a possibility;
(5) Surface finish might recast views on E.P. lubricants.

DISCUSSION.

Dr. K. O. Müller said that he wished to express his thanks for the opportunity to take part in the Summer Meeting, and he hoped that his English would be excused.

He had read the papers presented at the various sessions with great interest and appreciated the progress made during the last few years.

The Chairman's request that he should open the discussion was accepted as an honour which he was pleased to undertake.

With reference to motor oils, he still felt that more importance should be attached to the viscosity index or pole-height in connection with easy start at low temperatures. With reference to the physical and chemical characteristics to be determined in the

laboratory, his view was that alteration should first be devoted to the behaviour of oils in engines working under practical conditions; then from this a laboratory method should be devised—such as ageing tests—which would reproduce as closely as possible the alteration of oils in engines. An attack on those problems in that manner would show that physical data such as flash-point and laboratory pour point could be disregarded, as they had no bearing on practical conditions. They should, for example, be usefully replaced by viscosity measurements at low temperature and volatility.

He would also like to emphasize that lubricating oils should not always be blamed for unfavourable engine performance, for in his view the latter depended on the fuels, engine design, and metallurgy.

With regard to E.P. lubricants, he had experimented for many years with different testing machines such as the Timken 4-Ball, Almen, and S.A.E. types, but he had never found them to agree with each other, and their results did not, in his opinion, have any relation to practical operation.

At the same time, he would say that he had never been able to understand why those E.P. lubricants should ever have been needed. By that he meant, whilst the lubricants might be essential for certain designs of gears, those gears in themselves were really not essential, and it seemed to him that they existed solely for reasons of fashion. In other words, it was, as far as he believed, possible to give the vehicle the necessary free height above the road with worm-gears which could be so designed that their lubrication was provided by simple oils, and this dispensed with the need for complex lubricants having chemical corrosive effects.

The conditions for lubrication were obviously simpler if ordinary gears were robustly designed, provided adequate workmanship was put into the gears, and surface finish was carefully attended to. The preparation of surfaces would open up a new outlook, and deserved more attention.

Mr. C. H. Barton said that in the absence of Mr. Bouman, owing to military duties, he had been asked to say a few words about his paper. Mr. Bouman had emphasized two problems which were well known to all who were concerned with engine tests on lubricants. Those were the difficulty of obtaining reproducibility of observations and the variability of results with change of working conditions. The latter phenomenon gave rise to uncertainty in the interpretation of results, especially when data from one engine were applied to another. The reproducibility of results under constant test conditions was a necessary criterion of the validity of the observations.

With regard to ring-sticking at high cylinder temperatures in gasoline engines, he noticed that Messrs. McNicol, Williams, and Lamarque's heating test indicated that the tendency of a lubricating oil to give sticking increased with the volatility of the oil. In the course of the high-temperature ring-sticking experiments with engines, with which he had been concerned for about ten years, it had been found that the least volatile mineral oils—*e.g.*, bright stocks—were not outstandingly resistant to ring-sticking, as would be expected from their low volatility on the basis of Mr. Williams' results.

Of the various factors which controlled ring-sticking at high temperatures, the metals involved did not appear to exercise a marked influence. Thus, chromium-plated and nitrided cylinder liners gave about the same rapidity of ring-sticking as that with cast iron. Tinned rings also were comparable with cast iron ones in their behaviour under sticking conditions. He had also tried the addition of 0·5–1·0 per cent. nitrogen peroxide in the air/fuel mixture by dissolving the appropriate proportion of that compound in gasoline, but no effect on the rate of ring-sticking was found (cf. Hanson and Egerton, *Proc. Roy. Soc.*, Series **A**, **163**, p. 90, 1937).

The question of " varnish " deposition on the pistons of spark-ignited engines had been referred to in one or two of the papers at the meeting. He had had the opportunity of discussing that matter with several authorities when he was in America six months ago. The one point on which they seemed to agree was that the ill-effects of varnish occurred only during the early life of an engine, when piston-cylinder clearances were at a minimum, in causing the pistons to tighten up after the engine had been shut down. Some people considered that the varnish effect was greatest at low oil temperatures and with less chemically stable oils; and others that high oil temperatures were required to produce objectionable amounts of varnish. The number of instances in which varnish had actually caused running trouble was relatively few, and had been exaggerated by undue publicity.

MR. J. L. TAYLOR said that he was glad Dr. Pye had invited comments on the question of reproducibility when the engine was used as a testing unit, since it was well known that reproducibility was not easy.

He would also remind members that, in addition, engine tests were costly and laborious, so that cases could and did arise where engine design changed so rapidly that engine tests lost a great deal of their value by not being completed before the design became obsolete. He wished to stress, therefore, the necessity of endeavouring to obtain the maximum amount of information from a laboratory test, preferably one which was already well established, such as the British Air Ministry oxidation test. He was glad to learn from Dr. Pye that this was still considered a useful test to which to purchase aircraft-engine oils, and thought that its usefulness might be extended in the direction of determining ring-sticking tendencies of oils, and their liability to corrode newer bearing-metals, and also to form lacquer. Some information regarding the first of these properties might be obtained by observation of the occurrence or otherwise of nodules of carbonized or oxidized oil in a ring round the test-tube where the bubbles broke, and regarding the third property by the ease with which the tube could be cleaned by various solvents. As regards the second property, he thought that a determination of acidity, not necessarily total acidity by the conventional I.P.T. method, but rather water-soluble acidity, might be useful. He would like to hear whether other oil chemists had any observations on these suggestions.

There were some comments on one or two of the papers he wished to make. In the paper by Williams and co-workers on the suggested method for determining ring-sticking properties of oils, there was an apparent contradiction in ascribing maximum ring-sticking tendency in one instance to most volatile oils and in another instance to least volatile oils. He noticed, however, that the temperatures were different in the two cases, and thought possibly the test was one which was very sensitive to changes in temperature. As regards the observation that breakaway-force decreased with increasing sample, he thought this was to be expected since the ratio of air to oil was lower and, therefore, the oil would not be oxidized to such a great extent, and, on the other hand, there was more oil to dissolve its own oxidation products.

Lastly, in view of the comments made at the meeting on the effect of surface finish on, for example, "film-strength," he would like to read, for the benefit of those members who were not familiar with it, a part of the review he had made in the Institute's publication "Petroleum Technology in 1938." "A feature of the year's work is the attention given to the effect of the metal surface on wear. Improvements are claimed for surfaces chemically treated or finely finished. In the former case, by chemically treating bearing surfaces so as to dissolve selectively ferrite and other bodies considered as harmful detritus formed by attrition, Foster claims to produce a surface with a bearing capacity six times that of an untreated surface when tested with a straight mineral oil. The surface characteristics of cylinders and pistons should be conducive to polishing by small-sized abraded particles, says Teetor, claiming good results for the Ferrox method of surface treating. In the case of fine finishes papers have appeared by Sherman, working on the effect of surface finish on load carrying capacity, and by Connor, who relates surface roughness and oil consumption using a profilometer to study roughness. Sherman's figures are worth reproducing. Using the S.A.E. machine, he gets a figure of 117 lb. for a surface finish of 16–18 and of 217 lb. for a figure of 1–2 micro inches."

DR. A. VON PHILIPPOVICH said that it was impossible to get a good correlation between an oxidation test in the laboratory using all kinds of engines and oils, and working under varying conditions. In the D.V.L. much was being done to get repeatable results with engines and good correlation with laboratory tests.

When precautions such as measuring side clearance of piston rings to 0.001 mm., the blow-by from 20 : 20 seconds and so on, were taken, engine tests gave good repeatable figures. Tests on ring-sticking over a range of temperatures showed that there was a minimum time in which rings would stick. This minimum was not at the same temperature for different oils, and the form of the curve was also quite different. That showed that there was only a certain range in which ring-sticking was of importance. Above that range engine failure was due to non-lubrication (that meant volatility and lack of "oiliness"). Below that range sludging would be of greater importance.

In consequence of that, laboratory tests must also take into consideration a wide range of temperatures. Work carried out in France had shown that a coking test

at two different temperatures (oxidation at 150° C. and coking at 250–300° C.), when the coking was supposed to take place in the absence of oxygen, gave maxima which could account for the minima of ring-sticking time.

He thought it was worth mentioning that some valuable work on volatility seemed to have been forgotten. F. H. Garner published an article on the subject in *J. Instn Petrol. Tech.*, **7**, 98 (1921), and Hoblyn referred to a method of heating oil in a dish at 250° C. and measuring the volatility and the amount of asphaltic matter produced in *ibid.*, 1925, **11**, 1.

As a result of tests made by the D.V.L. it became apparent that nitrogen oxide had no specific influence in detonating combustion except by increased temperatures as a consequence of knocking.

Mr. H. J. Young said that it might have been overlooked that Robert Sulzer had read a paper on the subject of Piston and Piston Ring Temperatures in 1926, which appeared in Vol. 68 of the *Transactions of the Institute of Naval Architects*. Sulzer dealt with the temperatures, during the various strokes, of the piston, piston rings, and cylinder wall of a two-cycle marine diesel engine. In as far as he (Mr. Young) understood Sulzer's work, it showed that the top ring of the engine attained a maximum temperature lower than that of the top ring of a steam-jacketed steam engine; that the problem of overheating was confined mainly to two areas—namely, the surfaces of the top piston ring grooves and of the upper portions of the cylinder walls. Sulzer found that no thermal fluctuations took place at more than 5 mm. depth below the liner face, but that violent fluctuations occurred close to its working surface. He (Mr. Young) suggested that temperatures occurred which brought in other considerations concerning cylinder wear than those commonly discussed; for example, the effect of certain nascent carbonic oxides on metal momentarily almost molten.

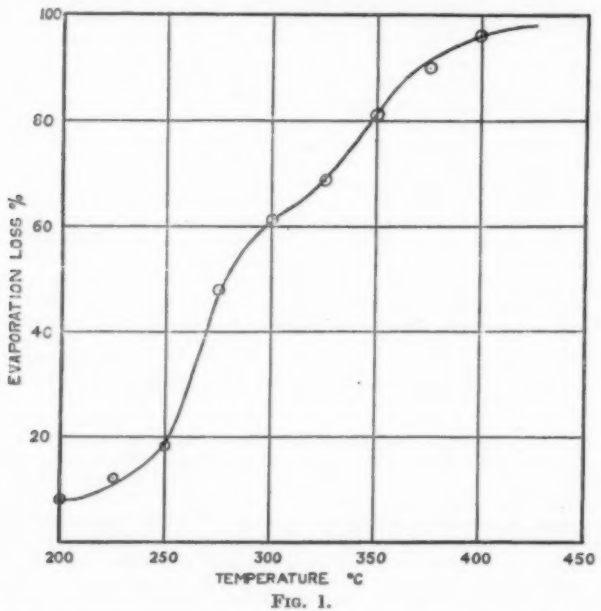


Fig. 1.

Dr. E. R. Redgrove said that he was glad to see that interest was being revived in film evaporation tests and the changes which took place during such tests.

About ten years ago he had a series of such tests conducted, and found that the evaporation curves were far from regular. A typical example was given in Fig. 1.

The " kink " in the curve was common to both distillates and blends of distillates and residual stock; the temperatures between which it occurred varied with the oil itself, the surface-area/volume ratio of the sample tested, and the volume of air passed over the surface of the sample. The treated samples were analysed for " Asphaltene " and " Carbene."

In all cases the " kink " appeared to be associated with serious decomposition of the oil, and it did not seem possible intelligently to interpret the results, which for that reason were not published. At that time ring-sticking and " varnish " or " laquer " were not the serious problem they were to-day, and in view of the present position he thought it might be advisable more closely to investigate the evaporation test over a wider range of temperature.

From the papers before the meeting and from the remarks of various speakers it was evidently appreciated that no one oxidation test could adequately foretell the behaviour of an oil under the varying conditions of temperature, nature, and composition of bearing surfaces and extraneous contamination which it was likely to encounter during service. He thought that nearly all sludging troubles were due to contamination from outside the crankcase, principally caused by incomplete combustion of the fuel, and only very slightly by decomposition of the lubricating oil film around the top rings.

With all those varying factors to contend with, it became necessary to adopt a control test for the chemical stability of a lubricating oil, and he thought the present Air Ministry test as good as any, provided that the asphaltic matter formed after oxidation was also determined and taken into account in assessing the merits of the oil tested.

Mr. J. Romney said that they had heard a great deal at that meeting about laboratory tests and service tests, and suggestions had been made that laboratory oxidation tests were not very useful, and did not accurately forecast the behaviour of oils in service. He would point out that it had been emphasized at that meeting that it was extremely difficult to reproduce engine results in duplicate tests even when all possible precautions were taken to control the conditions. This was not true of laboratory tests, and even complicated oxidation tests were, in general, capable of giving good agreement in duplicate determinations. It seemed reasonable, therefore, to select an oxidation test which was theoretically logical, and if its results could be directly correlated with those of a big series of service tests, to adopt it as a guide. That was what had been done by Mr. Wilford using the Air Ministry test in the laboratory and a very large number of vehicles on the road. He would make it clear, of course, that when he referred to the Air Ministry test, he was thinking of the actual oxidation method. Several people pointed out at yesterday's meeting how much more useful the test could be if asphalt development after oxidation was measured.

The point had been raised at that meeting that the value of the test could be further increased by measuring more properties of the oxidized oil, and the acidity had been mentioned as a probable reflex of the tendency towards corrosion. It might interest the meeting to know that he was concerned in some work on this particular point, and as far as their results went, it was impossible to correlate the acidity of the oil left in the oxidation tube with corrosion as reflected by the loss in weight of test-pieces immersed in the oil.

Mr. J. C. Jennings said he was particularly interested in the ingenious test described by McNicol, Williams, and Lamarque. It was rather difficult to decide to what extent it was a coking test, and to what extent it would be regarded as an oxidation test, but undoubtedly oxidation played an important part. It would be of interest to look into the effect of using different metals, active and inert, as well as glass, used as materials for the dishes, and to note whether the order in which different oils were rated by the test was in any way affected by the metal used. As a preliminary test it would probably be sufficient to compare the results already obtained with those obtainable on the same oils using copper dishes. He found the curve plotting evaporation loss against temperature (Fig. 5 of the same paper) rather surprising. It was practically a straight line, with a tendency towards flattening at the higher temperatures. He had had occasion recently to prepare curves of a similar type, but over the range 120–200° C. for a whole series of oils of different types, and these showed a very pronounced steepening at the higher temperatures. It seemed probable that in the case of the dish

test, oxidation and polymerization at the higher temperatures were a contributory factor.

Mr. Beale had referred to the almost phenomenal cleanliness and freedom from carbon of a crankcase oil which was being constantly filtered during service. It was difficult to explain the particular case which he quoted, but it was certainly a fact that removal of solid matter during service had an important effect. Some time ago his laboratory carried out a series of tests to study the effect of typical crankcase carbon. A sample of this was filtered off from a used oil and washed free from oil, and very small percentages were introduced into various new oils, which were then compared, on the Air Ministry oxidation test, with the uncontaminated oils. The effect was marked in every case, and quite considerable in some cases. In fact, results like double coke values and asphalt after oxidation were obtained in several cases with quite small percentages, even allowing for the added carbon to give a coke value and asphalt content of 10 per cent. These series of tests, of course, were a practical demonstration of the generally accepted opinion that the degradation of oils was an autocatalytic process, the products of reactions being catalysts for the progressive oxidation of the oil.

Mr. D. Clayton said that the effect of surface finish on the results with the Timken machine as described by Mr. J. H. Evans was very interesting, and supported the claims made by Chrysler for their "superfinish." This effect might explain some of the differences found between different extreme-pressure lubricant testing machines. It was noteworthy, however, that as regards coefficient of friction, and to some extent as regards load carried, all the tests with polished surfaces grouped themselves together and lay apart from those with ground surfaces; this suggested that, provided the surfaces were reasonably well polished, the degree would not be critical. It was thought that the explanation for the change with finish might lie in the formation of partial fluid film between the cup and the block. Support for this was found in Peppler's measurement of fluid film pressure in a machine of the Amsler wear-testing type,* and S. Way's explanation of pitting in a similar machine in terms of the hydrodynamic pressures.† Moreover results of Maag's were quoted on p. 742 showing the effect of viscosity. On the other hand, the impressions were shown to be not greatly different in size, and it would be interesting to know whether the appearance of the scars suggested any difference of régime.

The effect of plating on the behaviour was also interesting. The explanation might be in greater effective smoothness, or in different cohesional properties; little was known on the latter subject. There was a possible link here with the tin-plating of pistons, etc., where a difference of "pick-up" was found. This connection might be important; it was thought that the same fundamental phenomena were involved, viz. the transition from fine to course particle removal.

Messrs. Baxter, Snow, and Pierce also provided a similar link with cylinder operation as regards pre-treatment, as their work was closely related with some of the anti-scuffing treatment of piston-ring surfaces to facilitate running-in.

There was a noteworthy importance in this pre-treatment, because it would allow surfaces to be treated with extreme-pressure dopes which, though effective, could not be marketed on account of other qualities such as odour, instability, etc. On the other hand, as regards comparison with running-in treatments, the pre-treatment was not an alternative in so far as initial roughnesses were removed during running-in.

The small, rough impression found with the Timken machine was similar to that obtained in his (Mr. Clayton's) tests with the 4-ball apparatus when "mild" seizures occurred, and it had been found at one stage in the load range for powerful extreme-pressure lubricants (Fig. 5 (c)). It was curious that satisfactory running could be obtained under those conditions in view of the effects of finish shown by Mr. Evans.

With reference to the paper by Messrs. McNicol, Williams, and Lamarque, Mr. Clayton said it was unfortunate that any suggestions regarding the tests involved complication, as the present method was so delightfully simple. The tests described by Moutte, Dixmier, and Lion‡ indicated, however, the importance of low- as well as high-temperature treatment in affecting the type of oxidation product. Also immediate

* V.D.I. Forschungsheft No. 391, 1938.
† *Jl. App. Mech.—Trans. A.S.M.E.*, **2**, 1935, p. A49.
‡ *I. Mech. E.*, "General Discussion on Lubrication," 1937, vol. 2, p. 372.

high-temperature treatment prevented the volatile portion playing any part in the oxidation process.

The agreement with the service order of six lubricants as regards chemical stability, and the correspondence Mr. Wilford (p. 610) found between hard asphalt in service and in the Air Ministry oxidation test, indicated that correlation ought to be possible considering the new test as an oxidation test. A number of other dish tests had been made, *e.g.*, by the Bureau of Standards and by van Hinte (mentioned by Mr. Bouman), and it would be interesting to know whether there was any correspondence in the results. One of the obvious difficulties was the lack of knowledge of the oil used in each case, and they had there yet another example of the benefits that would accrue from the availability to all experimenters of two or three common reference oils.

Dr. H. Wright Baker wrote that Keyser and Miller, when speaking of cylinder wall temperatures had mentioned "another useful tool." He would go much further, and suggested that wall-temperature measurements, which could be made very simply, were essential to an understanding of many problems. The temperature of the coolant was almost useless as a guide to the temperature conditions or variations at the walls. A knowledge of piston temperatures, although much more difficult to obtain, was highly desirable, even if only to prevent the easy acceptance of theories which at first sight seemed obvious, but which were, in fact, frequently false.

The authors were to be congratulated on their contribution to the development of a simple and robust method of measurement which could be applied through long-period runs and which was largely free from the variables introduced by linkages, etc., in the piston mouth. Certain modifications might be suggested—for instance, the use of aluminium-constantan couples with aluminium pistons, coupled with a differential method of temperature measurement which would enable six contacts to serve for five couples instead of three.

It was to be regretted that although the method had been known for some years, the data regarding the apparatus were still so scanty—the drawings were published without any scale attached, and no mention was made of plunger mass and spring strength, which would probably be very relevant matters at really high speeds.

The same lack of data was very noticeable throughout the paper—for instance, Fig. 8 was published without reference to piston metal, and again without a scale, although the temperatures might vary with different pistons under the same test conditions and in the same engine from those which gave a very light varnish under the crown to others at which no carbonaceous deposit whatever could exist. He (Dr. Baker) could only recommend great caution in accepting the figures given in the paper until such time as the data necessary for their understanding were forthcoming.

A piston design was a compromise, but it should be a balanced compromise. Some of the worst cases of "lubrication" troubles would go when it was realized that one bright idea did not make a piston.

He hoped that the authors would continue their work of collecting and sifting facts, and would publish them with full details. There would be far less talk of "road tests" when they had taken the trouble to trace the variables which affected their problems. Engine tests were sufficiently complex without the introduction of chassis, road, weather, and personal factors. The importance of the temperature factor was very great.

Mr. J. H. Evans, in reply to the Discussion of his paper, wrote:

"As Mr. E. A. Evans points out in his summary of the papers, the term 'dope' is very loosely used to apply to extreme-pressure additives in both oils and greases, and it is preferable that such agents should be referred to as E.P. addition agents or E.P. bases.

Although having a preference for non-separating lime-soap greases for the general lubrication of Timken bearings, it was not intended to convey that all and sundry lime-soap greases were satisfactory and soda-soap greases unsatisfactory. Conditions of application must always be carefully considered and recommendations adjusted accordingly. As Evans stated, a rigid specification has been drawn up, but it is significant, from the long list of approved manufacturers, that the grease-makers can consistently meet the requirements of such specifications.

It is gratifying to learn that the Timken Stability Test has become both popular and

important, as this militates against the lone struggle that took place for such a long time.

In reply to Mr. D. Clayton, it is appreciated that variations in the surface finish may account for some of the differences between different E.P. testing machines. The question of surface finish of test components is very involved; experiments made on components which had been measured on the "Contoragraph" did not result in accordance with the rating of this instrument.

The effect of surface polish, as Clayton suggests, is to re-group the O.K. loads and coefficients of friction in a much higher plane than the ground components.

This helps to obtain uniformity of test components finish, but removes the comparison between testing machine and ordinary workshop finish of parts, unless 'Superfinish' becomes general practice for all ground or machined components.

The scars on the test blocks are shown in Plate I at their O.K. load.

Standard grind, fairly deeply worn scratched surface; I.F. similar appearance smaller area; O.D. and rouge small scars slight separated scratches.

With the exception of the standard grind, which showed the usual abrasive wear, the others consist of fine abrasive lines having very little depth."

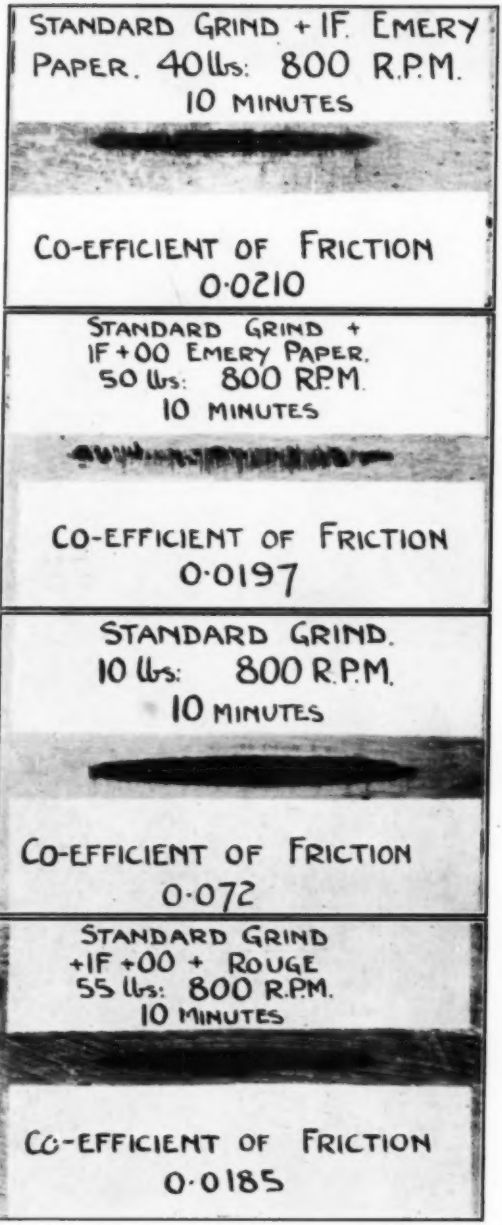

STANDARD GRIND + 1F. EMERY PAPER. 40 lbs: 800 R.P.M. 10 MINUTES
CO-EFFICIENT OF FRICTION 0·0210
STANDARD GRIND + 1F + 00 EMERY PAPER. 50 lbs: 800 R.P.M. 10 MINUTES
CO-EFFICIENT OF FRICTION 0·0197
STANDARD GRIND. 10 lbs: 800 R.P.M. 10 MINUTES
CO-EFFICIENT OF FRICTION 0·072
STANDARD GRIND +1F +00 + ROUGE 55 lbs: 800 R.P.M. 10 MINUTES
CO-EFFICIENT OF FRICTION 0·0185

PLATE I.

[*To face p.* 800.

PREPARATION OF SOME PURE HYDROCARBONS FOR THE PURPOSE OF TESTING THE PHYSICAL METHODS IN USE FOR THE EXAMINATION OF HYDROCARBON MIXTURES.* (PART I.)

By H. I. Waterman, Hon.M.Inst.Pet., J. J. Leendertse, A.M.Inst.Pet., and D. W. van Krevelen.

Introduction.

In the first paper on this subject,† attention was directed to the applicability, within narrow limits,[1] of the specific refraction molecular-weight method [2] to the determination of the elementary composition of saturated hydrocarbon mixtures. Proof for this applicability was furnished by comparing the results of a great number of elementary analyses of highly divergent mixtures of hydrocarbons of high molecular weight, with the results obtained from the application of the specific refraction method. Naturally, the limits of accuracy between which this check could be effected depend on the limit of accuracy of the elementary analysis. The latter, however, is not so great as the accuracy that can be reached in the determination of the specific refraction, so that for a complete test of the specific refraction method it is necessary to carry out a more exact check in some other way. This can only be achieved by preparing a number of pure hydrocarbons of different types, and testing the specific refraction method on these hydrocarbons and on mixtures of them.

Moreover, testing the specific parachor molecular-weight method [3] also requires a knowledge of the properties of a number of pure hydrocarbons of different types. It is known that, according to the latter method, an indication would be found in regard to the degree of branching of hydrocarbon mixtures, by comparing the cyclic character of the mixtures derived by means of the specific refraction method with the cyclic character obtained by the application of a specific parachor molecular-weight diagram evolved for this purpose. As a matter of fact, branched products show an excess of rings in the specific parachor diagram. The magnitude of this excess is a measure of the branching.

In view of the above, the authors intend to prepare a number of pure hydrocarbons of different types, of which those discussed in this paper are the first.

A description is given below of the preparation of pure normal octadecyl benzene, from which, by hydrogenation, pure octadecyl *cyclo*hexane could be obtained. It is on the latter substance that the above specific refraction and specific parachor molecular-weight methods were applied. The results obtained were approximately the same as those calculated for the pure substance concerned. Thus the hydrogen content derived from the observed specific refraction (0·3304) amounted to 14·49 per cent.,

* Paper received January, 1939.

† Compare "The Purity of some High Molecular Hydrocarbons as described in the Literature," by H. I. Waterman and J. J. Leendertse, *J. Instn Petr. Tech.*, 1939, 25, 89.

whilst on the strength of the constitution a hydrogen content of 14·38 per cent. was to be expected.

The octadecyl *cyclo*hexane, however, differed considerably from the product prepared by Mikeska.[5] As a by-product in the preparation of the octadecyl benzene, hexatriacontane was obtained. This latter product, too, was analysed after further purification.

Moreover, the specific refraction and specific parachor molecular-weight methods were applied to a synthetically prepared, not absolutely pure octyl *cyclo*hexane, and also to the hexadecane obtained as a by-product in the preparation of the former. For all these hydrocarbons the methods gave the results expected.

Description of the Investigation.

As base materials for the synthesis there were available normal primary octyl chloride, normal primary octadecyl chloride and bromobenzene, which were thoroughly purified. The original idea was to prepare the above aromatics, which, when carefully hydrogenated, could supply the desired saturated naphthenes, by making the Grignard compound of the chlorides or bromobenzene, and reacting this with bromobenzene or the chlorides, respectively. It was found possible, in fact, to make the Grignard compound concerned, but condensation with the corresponding component met with considerable difficulty, so that another method was adopted for the preparation. As such the Würtz–Fittig reaction was selected, in which, starting from a mixture of bromobenzene with the chlorides, the aromatic in question was formed. For preparing octyl benzene this reaction was carried out in the presence of ether; for preparing octadecyl benzene this dilution with ether could be omitted.

In addition to the reaction product desired, diphenyl (resulting from the reaction of 2 mols. of bromobenzene) and hexadecane and hexatriacontane, respectively (resulting from the combination of two chloride molecules), were also obtained in the reactions. Owing to these additional reactions the octyl benzene obtained could not be separated in an entirely pure state, as the impurities were very difficult to separate from the required product, due to the slight differences in the boiling points. The hexadecane preparation obtained as a by-product is to be considered as a *practically* pure product. Therefore, even if these preparations had no direct value for testing the specific refraction method, they were quite suitable for checking the specific parachor method, in so far as it consists in comparing the cyclic character of the products derived from the specific refraction and specific parachor molecular-weight graphs.

More favourable were the results obtained in the preparation of the octadecyl benzene and the hexatriacontane formed as a by-product in this preparation. In this case the additional reaction resulting in the formation of the paraffin was a very welcome one, as it ensured simultaneous, rapid, and reliable preparation of the hexatriacontane.

Besides the above additional reactions, which were expected, there was another reaction, although occurring to a slight extent only, which will be discussed later in greater detail.

Base Materials.

The bromobenzene used was a commercial preparation, purified by repeated subjection to sharp fractionation at atmospheric pressure. A preparation was finally obtained with a boiling point (760 mm.) of 155·2–155·9° C., $n_D^{20} = 1{\cdot}5599$, $d_4^{20} = 1{\cdot}4914$, molecular refraction 34·03 (calc. 34·07), and this was taken as a base material for the experiments.

As normal primary octyl chloride a preparation made by Fränkel and Landau was used (quality " purest "). Although its appearance was fairly pure, this product was also subjected to a repeated fractionation at atmospheric pressure. The final preparation used in the syntheses had the following constants: boiling point (755 mm.) 182·8–183·6° C., $n_D^{20} = 1{\cdot}4306$, $d_4^{20} = 0{\cdot}8704$, molecular refraction 44·15 (calc. 44·01), chlorine content 24·1 per cent. (calc. 23·9%).

The purity of this substance was further evidenced by the fact that its melting point was entirely constant and coincided with its solidifying point.

The normal primary octadecyl chloride, too, was a commercial preparation made by Fränkel and Landau, and it was also purified. In this case purification by distillation was not really practicable, as even when distilling under a considerably reduced pressure some decomposition was found to take place. Purification of this substance could, however, be effected by fractional crystallization. Finally, a preparation was obtained with a constant solidifying point, or melting point, respectively, of 19·5° C. The preparation had n_D^{39} 1·4450, n_D^{40} 1·4445, n_D^{41} 1·4440, d_4^{41} 0·8490, specific refraction (41°) 0·3129, (20° corrected) 0·3124 (calc. 0·3123).*

Preparation of Octyl Benzene, Octyl *cyclo*Hexane and Hexadecane.

34·5 gm. sodium wire were introduced into 250 cm.³ absolute ether, and, after cooling in ice-water, a mixture of 63 cm.³ bromobenzene and 124 cm.³ octyl chloride were added. The flask was then fitted with a Liebig cooler. After some time the sodium began to darken and heat was generated to such an extent that the ether began to boil and even partial distillation took place. When the reaction had proceeded for about 18 hrs., the excess sodium was decomposed with alcohol, the salts formed were dissolved in water, the ether layer was separated off, the water layer extracted with fresh ether, and the ether layer combined with the ether extracts dried on anhydrous Na_2SO_4. This complete treatment was repeated twice in exactly the same manner. After evaporation of the added ether, the total reaction product was subjected to distillation at 16 mm. In order to give an idea of the proportions in which the products had formed, the result of this first distillation is given below:

boiling point	40–70°	(16 mm.)	n_D^{20}	1·4260	about	80	cm.³
,, ,,	120–150°	,,	,,	1·4856	,,	130	,,
,, ,,	150–160°	,,	,,	1·4650	,,	40	,,
,, ,,	160–168°	,,	,,	1·4565	,,	20	,,

From this result we assumed that complete separation of the components

* A more exact proof for the structure of this base material will be given in a following paper.

by distillation would meet with serious difficulties. The fractions obtained were subjected to numerous redistillations, and finally 66 cm.^{3} of an "octyl benzene" preparation were obtained, with a boiling point of 140–144° C. (16 mm.). In view of the large boiling range, this is by no means to be considered as an entirely pure substance. The properties of the preparation are given in the table. Since a more satisfactory method of purification was not available in this case, the above product was used in the preparation of the "octyl *cyclo*hexane."

For this purpose the product was subjected to careful hydrogenation under high hydrogen pressure (initial pressure about 150 kilos/cm.^{2}), in the presence of 10 per cent. nickel catalyst (nickel on kieselguhr), the temperature remaining below 200° C. for the greater part of the hydrogenation. Only when the product was almost completely saturated was the temperature raised for some time above 200° C. (maximum 255° C.). The constants of the product thus obtained were determined; they are also given in the table.

The higher-boiling fractions of the reaction product of the Würtz–Fittig reaction were expected to consist essentially of hexadecane. Actually in the above fractionations of the reaction mixture two fractions were separated, the properties of which approximated those of hexadecane as mentioned in the literature, but which possibly still contained some octyl benzene, an impurity which is very difficult to separate from it by distillation.

Besides this, however, another impurity had to be considered; when determining the bromine number of one of the "hexadecane fractions," it showed a certain degree of unsaturation, pointing to the presence of olefinic double bonds. By treating the preparations with concentrated sulphuric acid and subsequently separating them with 5 per cent. fuming sulphuric acid and subjecting them to sharp fractionation, the products shown in the table as hexadecane I and hexadecane II are finally obtained.

In view of the process adopted, the hexadecane II is to be considered as the purest hexadecane preparation made by us; it had a constant melting point and solidifying point coinciding with each other. The other properties tallied well with those of the pure normal hexadecane described by Van Westen. Therefore, at any rate, the conclusion is justified that the hexadecane II is to be considered as a practically pure normal hexadecane.

The discovery of slight unsaturation due to olefinic double bonds in one of the "hexadecane" preparations led us to consider the Würtz–Fittig reaction in greater detail.

In order to find out whether the formation of the unsaturated compounds was caused by a possible splitting off of hydrocloric acid from the octyl chloride, the latter was made to react with sodium using ether as a medium, in a manner comparable with the process adopted when octyl benzene was formed. In the distillation of the reaction product first runnings were indeed found to be present, containing, in addition to unconverted octyl chloride and octene, also octane. The "hexadecane" separated by distillation also proved to contain a small amount of olefine (bromine number, according to McIlhiney, 8·5). Therefore, in the reactions in which octyl chloride enters into contact with sodium under the conditions referred to above, it appears that we have to consider a reaction comparable with that in which hydrochloric acid is split off, octene being formed at the same time. This

octene might then be hydrogenated to normal octane by the hydrogen formed from sodium and the acid, whilst another part of the octene might have formed the hexadecene by polymerization; the latter might be partly recovered directly in the form of hexadecane by hydrogenation. The possibility of a branched hexadecene being formed partly when the octene is polymerized as stated above must not be precluded. On the other hand, the agreement found between the hexadecane II and the preparation made by Van Westen (see table) in quite a different way, and renders the presence of branched hydrocarbons in the preparations used for checking purposes highly improbable. Moreover, if the reaction scheme drawn up by Schlubach and Goes [4] for analogous reactions described in the literature should also hold good for this case, the formation of branched hydrocarbons would be out of the question.

Finally it may be stated that high-pressure hydrogenation was carefully carried out on the hexadecene–hexadecane mixture obtained, with nickel as a catalyst, the highest temperature being 162° C. The product found has been called hexadecane III in the tables. Although this preparation was not purified with the same care as the previous hexadecane preparations, the specific refraction and the specific parachor prove to tally practically entirely with those of the other hexadecane preparations.

Preparation of Octadecyl Benzene, Octadecyl *cyclo*Hexane and Hexatriacontane.

For the preparation of octadecyl benzene the base material consisted of 62·5 gm. sodium wire, 133·5 gm. bromobenzene and 350 gm. octadecyl chloride. Immediately after the sodium was introduced, the flask was placed in ice water and provided with a reflux cooler. In this case the reaction was slow; after the flask had been left to stand at low temperature for some 18 hours, in order to carry through the reaction as far as possible, the whole was heated up to 150° C. Thereupon the unconverted sodium was decomposed with alcohol, the separated salts dissolved in water, and the water layer extracted with fresh ether. In this treatment part of the reaction product remained undissolved; a large quantity of solid organic matter was left. This product was filtered off, 70 gm. of a substance with a melting point of 72° C. being separated.

The portion soluble in ether was distilled, first under atmospheric pressure to remove the ether, then at a pressure of 2 mm. First 8 gm. distillate were obtained, then 75 gm. unconverted octadecyl chloride (boiling point 175–190°, 2 mm.), and the rest distilled over almost completely at 212–216° C. The latter substance was the octadecyl benzene, of which some 70 gm. were obtained. This impure octadecyl benzene was purified by repeatedly subjecting it to crystallization. The best process that could be adopted for this purpose was dissolving the substance in ether and precipitating it again from the ether solution by means of methanol. This was repeated until the melting point remained entirely constant. The product thus obtained was a pure white powder. The constants are shown in the table, in which the data found by Mikeska are also mentioned.

This octadecyl benzene was used for the preparation of pure octadecyl *cyclo*hexane. To this end the substance was subjected to careful hydro-

genation under high hydrogen pressure and with nickel catalyst, in the same way as mentioned for the preparation of the octyl *cyclo*hexane. The maximum temperature in this case was 260° C.*

Compound.	n^t_D.		$d^{20}/_4$.		r^t_D.		r^{20}_D. Theoretical.	Aniline Point. °C.		Molecular Weight.	
	n_D.	t° C.	d.	t° C.	r_D.	t° C.		Observed.	From Graph.	Observed.	Theoretical.
"*n*-Octyl benzene"	1·4890	20	0·8622	20	0·3348	20	—	< − 5	—	—	190·18
"Octyl *cyclo*hexane"	1·4515 1·4311	20 70·3	0·8165 0·7822	20 70·3	0·3301 0·3310	20 70·3	0·3294 —	74·7		195	196·22
"Hexadecane" I	1·4354	20	0·7752	20	0·3369	20	0·3363	—	—	—	—
"Hexadecane" II	1·4351	20	0·7746	20	0·3369	20	0·3363	95·0	95	—	—
"Hexadecane" III	1·4345	20	0·7742	20	0·3367	20	0·3363	—	—	—	—
Hexadecane literature	1·4352 [a]	20	0·7751 [a]	20	0·3368 [a]	20	0·3363	—	—	—	—
Octadecyl benzene	1·4778 1·4768 1·4745 1·4730 1·4640 1·4600	27 30 36 40 63 73·5	0·8437 0·8224	41 71·5	0·3322 0·3335 (extra-pol.) 0·3313	41 71·5 20	—	50·7	—	—	330·33
Octadecyl benzene literature	1·4812 [c]	25	0·8540 [c]	25	0·3333 [c] (calc.)	25	—	47·0 [c]	—	—	—
Octadecyl *cyclo*hexane	1·4555 1·4542 1·4522 1·4500 1·4420	33·8 38 43 49 70·3	0·8126 0·7983	48 70·3	0·3310 0·3315 0·3304 (extr.)	48 70·3 20	0·3294	106·7	106	—	336·38
Octadecyl *cyclo*hexane literature	1·4538 [c]	25	0·8340 [c]	25	0·3246 [c] (calc.) 0·3245 (extr.)	25 20	0·3294	—	—	—	—
Hexatriacontane	1·4359 1·4349 1·4341 1·4316 1·4313	77 80 82 88 89	0·7795 0·7671	82 100	0·3341 0·3348 0·3319 [b] (extr.)	82 100 20	0·3325	132·8	126	—	506·59
Hexatriacontane literature	—	—	0·7819 [d]	78	—	—	—	—	—	—	—

[a] H. A. v. Westen, Thesis, Delft, 1931, p. 70. H. I. Waterman, P. van 't Spijker, and H. A. van Westen, *Rec. trav. chim.*, 1929, **48**, 1103.
[b] P. C. Carey and J. C. Smith, *J. chem. Soc.*, 1933, 346.
[c] L. A. Mikeska, *Ind. Eng. Chem.*, 1936, **28**, 970.
[d] F. Krafft, *Ber.*, 1907, **40**, 4779.
[e] Gascard, *Compt. rend.*, 1911, **153**, 1486.

The reaction product of the hydrogenation was recrystallized in the same way as described for the corresponding unsaturated product. The

* It has since been proved that this hydrogenation at high temperature in the presence of nickel catalyst has not caused undesired side-reactions (compare H. I. Waterman, J. J. Leendertse, and J. F. Sirks "Preparation of some Pure Hydrocarbons, etc.", Part II, p. 809.

substance finally obtained consisted of small leaves with a silvery lustre, the properties of which are shown in the table, together with the constants mentioned by Mikeska.

Surface Tension [f] t° C.		Specific Parachor.		Specific Parachor from graph.	Specific Dispersion × 10^4.	Number of rings per molecule.			Boiling Point, ° C.	Melting Point, ° C.	Halogen Content, %.	
σ(dyne/cm.).	t° C.	p.	t° C.			From r_D^{20}.	p^{20}.	Theoretical.				
30·59	20	2·728	20	—	239	—	—	—	140–144 (16 mm.)	—	—	The authors' preparations
29·17	20	2·846	20	2·846	154·5 (70·3)	0·9	1	1	—	—	0	
27·66	20	2·959	20	2·962	—	−0·1	0	0	160–162 (15 mm.)	17·0	—	The authors' preparations
27·67	20	2·961	20	2·962	—	−0·1	0	0	157–158 (15 mm.)	17·8	—	
27·50	20	2·958	20	2·962	—	−0·05	0	0	—	14·8	—	
—	—	—	—	—	—	−0·1	—	0	—	18·13 [b]	—	
										17·8 [a]		
30·85	50	2·815	50									The authors' preparation
28·88	71·5	2·819	71·5	—	—	—	—	—	—	32·8	—	
		2·809 (extr.)	20									
—	—	—	—	—	—	—	—	—	—	35–36 [c]	—	
29·75	48	2·874	48		153	0·8	0·9	1	—	40·7–40·8	0	The authors' preparation
28·26	70·5	2·889	70·5									
		2·855 (extr.)	20	2·847								
—	—	—	—	—	—	2·0	—	1	—	40 [c]	—	
27·48	84	2·943	84		—	(0·2) [h]	(0·2) [h]	0	—	76·0	0	The authors' preparation
26·59	98	2·955	98									
		2·888 [h] (extr.)	20	2·901								
—	—	—	—	—	—	—	—	—	—	about 76·0 [d]	—	
										76·0 [e]		
										76·5 [f]		
										78·5 [g]		

[f] A. Oskerko, *Chem. Zentr.*, 1914, II, 1265.
[g] P. A. Levene, C. J. West, and J. v. d. Scheer, ref. in *Brit. Chem. Abstr.*, 1915, **34**, 634.
[h] Extrapolated over a wide temperature range, and therefore not very accurate.
[i] The determinations were made by the stalagmometric method.
[j] This preparation did not contain any sulphur.

Finally it was necessary to further purify the solid substance, only slightly soluble in ether, which was separated from the total reaction product and which, in view of the way in which it was formed, may be considered to be impure hexatriacontane. This product, coloured slightly brown, was recrystallized a few times from petroleum ether, after the solution had been treated with norite. Finally the melting point became

constant at 76·0° C. The product consisted of pure white leaves and was fairly readily soluble in warm petroleum ether and warm benzene, but soluble with difficulty in ether and alcohol. The constants of this substance are also given in the table.

It may be remarked that in this synthesis no indications were found of the formation of olefinic unsaturated compounds.

Consideration of the Results Obtained.

It follows from the results obtained that for the compounds considered the number of rings per molecule may be derived from the specific refraction, with an accuracy of at least 0·2 ring per molecule.

For the calculation of the specific refraction of hexatriacontane at 20° C. it was necessary to extrapolate over a very large temperature range, therefore in this case the latter specific refraction value may be somewhat less accurate than for the octadecyl *cyclo*hexane. Yet the results obtained could still be qualified as highly satisfactory, as the specific refraction gave an indication of 14·66 per cent. hydrogen, whilst from the constitution 14·72 per cent. might be expected.

It is apparent from the specific parachor values found that the specific parachor tallies well with the specific parachor molecular-weight diagram previously drawn up. Here, too, the result for hexatriacontane is slightly less accurate than for the other compounds, owing to the large extrapolation required for calculating the specific parachor at 20° C.

When two compounds of a homologous series differing appreciably in molecular weight correspond in properties, it is not probable that the other compounds belonging to this series will show deviations, therefore we may consider this check as a check on the curve of the unbranched paraffins and on the curve of the monocyclic six-ring naphthenes with only one unbranched side-chain. For the compounds in question, when calculating the number of tertiary C atoms by a comparison of the number of rings per molecule derived from the specific refraction and also from the specific parachor, about 1 tertiary C atom would be found, which, within the limits of accuracy of observational error, agrees with the actual content.

References.

[1] H. I. Waterman and J. J. Leendertse, *Chimie et Industrie*, numéro spécial congrès Paris, September 1937.
[2] J. C. Vlugter, H. I. Waterman, and H. A. van Westen, *J. Instn Petr. Tech.*, 1935, **21**, 661.
[3] H. I. Waterman and J. J. Leendertse, *ibid.*, 1938, **24**, 16.
[4] H. H. Schlubach and E. C. Goes, *Ber.*, 1922, **55**, 2889.
[5] L. A. Mikeska, *Ind. Eng. Chem.*, 1936, **28**, 970.

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PREPARATION OF SOME PURE HYDROCARBONS FOR THE PURPOSE OF TESTING THE PHYSICAL METHODS IN USE FOR THE EXAMINATION OF HYDROCARBON MIXTURES.* (PART II.)

By H. I. Waterman, Hon.M.Inst.Pet., J. J. Leendertse, A.M.Inst.Pet., and J. F. Sirks.

Summary.

The *n*-octadecyl*cyclo*hexane prepared in a pure state from *cyclo*hexyl iodide and octadecyl chloride has been shown to be identical with the *n*-octadecyl*cyclo*hexane prepared from *n*-octadecyl benzene by hydrogenation at 200–260° C., using high-pressure hydrogen and nickel-on-kieselguhr as a catalyst.[1] Thus, hydrogenation under these conditions did not cause undesirable structural changes. This fact is of general interest, because similar hydrogenations are often carried out in the analysis of hydrocarbon oils using the specific refraction–molecular weight method.[2]

Introduction.

The synthesis of pure *n*-octadecyl*cyclo*hexane has been described in a previous paper.[1] For the preparation of this compound, the Wurtz–Fittig condensation of normal primary octadecyl chloride and bromobenzene was used, followed by purification of the octadecyl benzene. In order to obtain *n*-octadecyl*cyclo*hexane from the octadecyl benzene, the latter substance was hydrogenated at about 200–260° C., using high-pressure hydrogenation and nickel-on-kieselguhr as catalyst. After two recrystallizations of the hydrogen product (yield of these recrystallizations more than 90 per cent.), the resultant compound was considered to be pure *n*-octadecyl-*cyclo*hexane.

However, during the course of hydrogenation, owing to the relatively high temperature and the presence of nickel catalyst, it is possible that isomerization or other structural changes might have taken place during the reaction. In order, therefore, to prove the reliability of the method of preparation of *n*-octadecyl*cyclo*hexane, previously described,[1] the authors decided to synthesize the same compound in another way, avoiding hydrogenation at high temperatures—namely, by the condensation of *cyclo*hexyl iodide and *n*-octadecyl chloride, using metallic sodium.

The condensation product agreed very well with the *n*-octadecyl*cyclo*-hexane previously described,[1] and it was therefore concluded that the structure of *n*-octadecyl benzene had not been changed by hydrogenation. This fact is also of general interest, in view of the fact that similar hydrogenations are often carried out in the analysis of hydrocarbon oils using the specific refraction–molecular weight method.[2]

Experimental.

The method of preparation of *n*-octadecyl*cyclo*hexane described below is similar to the method recently [1] followed for the synthesis of pure

* Paper received January 1939.

n-octadecyl benzene. *cyclo*Hexyl iodide was, however, used instead of bromobenzene. (*cyclo*Hexyl bromide could not be used, as the yields proved to be very poor.)

The base material " normal primary octadecyl chloride " was a commercial product made by Fränkel and Landau (quality " reinst "), similar to the preparation used in the experiments previously described.[1] It was recrystallized once. [After recrystallization : $n_D^{25} = 1{\cdot}4509$; $d_4^{25} = 0{\cdot}8579$; specific refraction (25° C.) = 0·3137, (calculated for $C_{18}H_{37}Cl$) 0·3123; melting point = 19·4° C.]

The *cyclo*hexyl iodide was prepared by interaction of equimolar quantities of *cyclo*hexanol (Fränkel and Landau, quality " reinst "), and a 70 per cent. hydriodic acid solution at room temperature, followed by heating at 105° C. for 1½ hour, the reaction mixture being stirred. The lower layer of the reaction product was washed with a potassium hydroxide and a sodium thiosulphate solution. After drying over anhydrous Na_2SO_4, it was distilled. A fraction with boiling point 33° C. (1 mm.) and n_D^{20} 1·548 was used in the experiment, although it was probably contaminated with some *cyclo*hexanol.

The condensation experiment was carried out in a 1-l. round flask with reflux cooler. 14·2 g. sodium (wire) were introduced in the (cooled) mixture of 52 g. *cyclo*hexyl iodide and 71·5 g. octadecyl chloride. The reaction temperature was kept at about 60° C. during the main part of the reaction. When the condensation was nearly finished the whole was heated at 130° C. for 1 hour.

After cooling, the unconverted sodium was decomposed with alcohol, the separated inorganic salts, the alcohol, etc., dissolved in water, and the water layer, as well as the hydrocarbon layer, extracted with cold ether. In this treatment a part (25·5 g.) of the product remained undissolved. Probably this part (melting point 75° C.) consisted mainly of hexatriacontane, obtained by the reaction of 2 mols. of *n*-octadecyl chloride (compare also [1]).

The solution of the hydrocarbons in ether was dried over anhydrous Na_2SO_4 and distilled first under atmospheric pressure to remove the ether, and then at a pressure of 1–2 mm. The result of this distillation is summarized in Table I.

TABLE I.

Fraction Number.	Quantity, g.	Boiling Temp., ° C.	Distillation Pressure, mm.	n_D.	Melting Point, ° C.	Remarks.
I	6·5	80–95	1–2	1·4757 (20°)	—	Dicyclohexyl?
II	16·5	144–149	„	1·4368 (35·2°)	24·7	Probably mainly octadecane and octadecene
III	1	149–184	„	—	—	—
IV	20·5	184–190	„	1·4538 (40°)	38·8	Octadecylcyclohexane
Residue	5	> 190	„	—	—	—

The melting point and n_D values of the fourth fraction are practically the same as those for pure octadecyl*cyclo*hexane (compare [1]). This fraction was purified by several recrystallizations, the first time by dissolving it in ether and precipitating it from the ether solution by means of methanol,

TABLE II.

Octadecylcyclohexane.

Product from	n^t_D.		d^t_4.		Specific Refraction.		Surface Tension.		Specific Parachor.		Solidifying Point, ° C.	Specific Dispersion.*	Number of Rings per Molecule.		
	n_D.	t° C.	d.	t° C.	r^t_D.	t° C.	σ_t (dyne/cm.).	t° C.	p_t.	t° C.			from r_D.	from p_{20}.	Theoretical Value.
Octadecylbenzene, prepared by D. W. van Krevelen.[1]	1·4504 1·4420	48 70·3	0·8126 0·7983	48 70·3	0·3310 0·3315 0·3304	48 70·3 20	29·75 28·26	48 70·5	2·874 2·889 2·855 (extra-pol.)	48 70·5 20	40·7–40·8	153	0·8	0·9	1·0
Octadecylchloride and *cyclo*hexyl iodide prepared by J. F. Sirks.	1·4503 1·4423	48 70	0·8124 0·7983	48 70	0·3310 0·3316 0·3302	48 70 20	29·80	48	2·876 2·857 (extra-pol.)	48 20	40·9	152	0·8	0·9	1·0

* $\frac{n_{F'} - n_C}{d} \times 10^4$.

followed by simple recrystallizations from ether as such. These recrystallization experiments were continued until the physical constants remained practically constant, which was the case after four recrystallizations.

In Table II the physical constants of the final product are compared with those previously described.[1] The figures in this table clearly indicate that the two preparations prepared by two investigators using different methods of synthesis are identical.* It can therefore be concluded that the hydrogenation of pure *n*-octadecylbenzene at 200–260° C. using high-pressure hydrogen and nickel-on-kieselguhr as catalyst has not changed the original structure of this hydrocarbon. Moreover, the agreement between the physical constants of both products is valuable evidence of the accuracy of the constants for pure *n*-octadecyl benzene and *n*-octadecyl*cyclo*hexane, previously described.[1]

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[1] H. I. Waterman, J. J. Leendertse, and D. W. van Krevelen, *J. Instn Petrol.*, 1939, **25**, 805.
[2] J. C. Vlugter, H. I. Waterman, and H. A. Van Westen, *J. Instn Petrol. Tech.*, 1935, **21**, 661.

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* It may also be noted that the melting point of a mixture of equal quantities of the preparations of Sirks and van Krevelen [1] agreed completely with the melting points of these individual samples.

CORRESPONDENCE.

THE ANALYSIS OF THE KEROGEN OF OIL SHALES.*

Mr. F. W. Quass (*Fuel Research Institute of South Africa*) writes :

Incidental to some work being undertaken at the Fuel Research Institute of South Africa, it has been necessary to attempt the reduction of the mineral matter of certain coals and oil shales (torbanites). The nature and the object of the research made it impossible to use acid extraction as carried out by Dr. Down. By applying a method based on the Trent Amalgamation Process, success has been achieved in removing the greater portion of the mineral matter from these samples.

The method is briefly as follows : A sample of the torbanite is very finely ground with water in a porcelain ball mill and then transferred to a porcelain end-runner, where a quantity of oil is added. All the torbanite, after grinding, passes through 200 mesh, and the average particle size is very much smaller. At this stage the mass consists of 50 gms. of torbanite, 200 c.c. of water and 60–70 c.c. of oil. The oil forms a paste with the carbonaceous material, and the greater portion of the mineral matter remains suspended in the water and can be separated. The separation of low-ash carbonaceous material from the mineral matter is complete, the mineral matter showing no trace of dark colour. The oil-paste is thoroughly cleaned by washing with water while agitating it by means of an egg-beater. The oil is then removed by washing the paste with hot petrol and finally with carbon tetrachloride. The first separation is extremely efficient, reducing the ash content of South African torbanite from 40 per cent. to about 10 per cent. The process, however, may be repeated successfully, and eventually a minimum ash content is obtained. This minimum figure is reproducible, and may be provisionally regarded as representing the " organic " or " inherent " mineral matter content of the torbanite.

Analyses of two samples of torbanite before and after treatment are given below in Tables A and B.

Table A.

Proximate Analysis.

	Sample 1.		Sample 2.	
	Whole.	De-ashed.	Whole.	De-ashed.
% Moisture	0·9	4·2	1·2	1·7
% Ash	31·2	9·7	37·6	4·9
% Volatile Matter	49·9	61·0	42·7	62·5
% Fixed Carbon	18·0	25·1	18·5	30·9
% V.M. (Dry ash-free)	73·5	70·8	69·8	66·9

In Table A it is noticed that the percentage of volatile matter calculated on the dry, ash-free torbanite decreases on the treated samples.

* Paper by A. L. Down, D.Sc., in the April 1939 issue of the Journal (pp. 230–237).

TABLE B.
Ultimate Analysis.

	Sample 1.		Sample 2.	
	Whole.	De-ashed.	Whole.	De-ashed.
% Carbon D.A.F.	80·3	85·9	79·2	83·0
% Hydrogen D.A.F.	9·16	9·00	8·52	8·27
% Oxygen D.A.F.	8·2	3·1	8·2	6·1
C/H ratio	8·8	9·5	9·3	10·0
C/O ratio	9·8	27·7	9·7	13·6

The ultimate analyses indicate that similar conclusions to those reached by Dr. Down can be made, namely :—

(1) the percentage of carbon is higher in the treated samples,
(2) the percentages of hydrogen and oxygen are lower in the de-ashed samples, and
(3) the ratios of carbon to hydrogen and carbon to oxygen have increased in these de-ashed torbanite samples.

At present the solution offered by Dr. Down—viz., that the unknown amount of water of hydration of the mineral matter associated with the torbanite makes the ultimate analysis, as determined on the original samples, contain errors of considerable magnitude—seems the most feasible explanation of the anomalous results given in Tables A and B. From Table A it will be noted that the volatile matter content of the de-ashed torbanite is less than that for the original, and it seems a pity that Dr. Down did not carry out volatile matter determinations on the de-ashed samples as well as on his air-dried samples. This decrease follows also quite logically from the solution given above.

If, however, the liquids used to wash the oil out of the paste dissolve part of the organic material of the torbanite, the effect on the ultimate analysis of the samples would be a tendency to give higher carbon and oxygen and lower hydrogen contents, since the material extracted is likely to be rich in hydrocarbons of a high hydrogen content. For similar reasons the volatile matter content should decrease.

No study of this possibility with South African torbanites has as yet been made, and it must be recognized that the above argument cannot explain the remarkable decrease in the oxygen content of the de-ashed samples unless very large quantities indeed of extract are removed by the solvents.

Altogether, at this stage it is felt that the order of any effects due to solution is insufficient to account for the differences which obtain, and preference is given to the explanation advanced by Dr. Down.

Dr. G. W. HIMUS (*Elveden Fuel Laboratories, Imperial College, London*) writes :—

MR. Quass is to be congratulated on having worked out a method of reducing the mineral content of oil-shale by a physical method which can be conveniently applied to considerable quantities of material, while at the same time it should be possible to make a substantially quantitative separa-

tion of the kerogen from the mineral matter, the latter being recovered in such a condition that it can be examined in detail. The process of removing the mineral matter by means of treatments with acids (A. L. Down, *Journal Inst. Petroleum*, 1939, **25**, 230–237) suffers from the inherent disadvantages that it is costly and difficult to apply to more than 30 to 50 gms. of sample at one time, and also that during the treatment with hydrofluoric acid to remove silica, the silica is not easily recoverable,; consequently, it is generally not feasible to carry out a weight-balance throughout the de-ashing.

It would be a matter of interest if Mr. Quass would give quantitative data (*a*) as to the percentages of kerogen and mineral matter recovered from his specimens and also (*b*) as to the nature of the mineral matter separated. The statement that the mineral matter showed no traces of dark colour is insufficient and might well be amplified.

While, however, the practical value of Mr. Quass' work is not in question, there are one or two statements in his communication which are open to criticism. Mr. Quass speaks of " the anomalous results given in Tables A and B." The " anomalous results " presumably are the differences in the compositions of the dry, ashless materials as calculated from the analyses of the " whole " and the de-ashed samples, and he directs attention more particularly to higher carbon and the " remarkable decrease in the oxygen content of the de-ashed samples."

In point of fact there is no anomaly in the results; the calculation of the composition of a solid fuel on a " dry, ash-free " basis is really an attempt to arrive at the true composition of the organic matter in the fuel—*i.e.*, free from moisture and *mineral matter*. But, inasmuch as the ash as determined by incineration is invariably less in quantity and different in composition from the original mineral matter, the composition of the organic component of the fuel as calculated " ash-free " will always differ from the true composition, the difference being a function of the mineral content of the sample on which the analysis was carried out. The errors introduced by this difference between the percentages of ash as determined by incineration and original mineral matter, *plus* small errors inherent in any analysis, are summed in the " oxygen " figure which is arrived at by deducting from 100 the total of the carbon, hydrogen, nitrogen, sulphur, and ash. " Oxygen " should be reported as " oxygen by difference " or (better) " oxygen *plus* errors," and, as Mr. Quass' results show, the " oxygen *plus* errors " may consist chiefly of errors with a little oxygen thrown in as a makeweight. If, however, prior to carrying out an analysis, the fuel is treated so as to reduce the ash to (say) 2 per cent. or less, the errors are reduced, so that the final composition as calculated is a very close approximation to that of the pure organic matter.

Mr. Quass also remarks that Dr. Down's suggestion " that the unknown amount of water of hydration of the mineral matter associated with the torbanite makes the ultimate analysis, as determined on the original samples, contain errors of considerable magnitude—seems the most feasible explanation of the anomalous results given in Tables A and B."

At the outset of the research at the Imperial College, it was realized that until the uncertainties resulting from the presence of unknown quantities of hydrated minerals containing unknown amounts of combined water could

be eliminated, it was hopeless to expect to be able to determine either the percentage of kerogen in a shale or its composition. The de-ashing process described by Dr. Down was therefore devised, and is now applied (with suitable modification, where necessary) to all samples of oil-shale which are to be investigated.

Mr. Quass very properly refers to the possibility that some of the kerogen may be removed in solution by the oil during the de-ashing treatment. While this danger is a real one, it should be possible to ascertain by experiment whether with any particular sample such an error is likely to be introduced, and then to guard against it by suitable modification of the treatment.

The above remarks are not offered in any spirit of carping criticism; Mr. Quass has worked out a method which will place in the hands of research workers a valuable weapon whereby they may overcome the inherent difficulty arising from the association in oil-shales of (often) a relatively small quantity of kerogen with a large proportion of mineral matter. By the application of this " amalgamation " process it should be possible to separate the kerogen from the mineral matter in an oil-shale, so that each constituent may be thoroughly studied both qualitatively and quantitatively.

Dr. A. L. Down (*Department of Chemical Technology, Imperial College, London*) writes :—

The success of a physical method for separating the kerogen from the mineral matter of an oil shale or torbanite is of considerable importance, since, as compared with processes involving treatment with mineral acids, it has the advantages that larger amounts of material can be treated and the possibility of any chemical alteration of the organic matter being effected by the reagents is eliminated. A. E. Flynn [1] employed a flotation method for isolating " kerogen globules "—*i.e.*, algal colonies—from " stellarite," a Nova Scotia torbanite, but the product contained 13·85 per cent. mineral matter, and the results showed that there had been a differential separation of the organic material, the gangue having about 25 per cent. of organic matter, of much lower " volatile matter " to " fixed carbon " ratio, associated with it. In the preliminary investigation of de-ashing at the Imperial College the " float-and-sink " test for the washability of coals was applied to a sample of South African torbanite, ground to pass a 90-mesh sieve, and practically no separation was obtained, the lightest fraction having approximately 30 per cent. of ash and the heaviest 50 per cent. The success achieved at Pretoria, therefore, shows the importance of very fine grinding if physical means of separation are to be used; further, it indicates the fineness of the original material and the intimate mixing of the organic and inorganic constituents.

The method employed by Mr. Quass has the disadvantage that the part of the kerogen soluble in organic solvents is removed; extraction of South African torbanite with acetone yielded 1·6 per cent. by weight of the kerogen and with chloroform 0·9 per cent. The soluble material is considered to be mainly hydrocarbons; J. W. McKinney [2] examined the acetone extract from a New Brunswick oil shale and found it to contain 85 per cent. of hydrocarbons. As A. J. Carlson [3] has shown, there is the possibility that

part of the kerogen is combined in some way, either physical or chemical, with the mineral matter. Solvent extraction of substantially de-ashed samples of Kimeridge and Middle Dunnet oil shales showed that the amounts of soluble material, calculated as percentage kerogen, were higher than those obtained from the untreated shales.

	Acetone Extraction.	
	Oil Shale.	De-ashed Sample.
Kimeridge	4·22%	6·45%
Middle Dunnet	5·69%	8·97%

The extracts are given as percentage of kerogen.

The results suggested that either part of the organic matter was physically combined with the mineral constituents, or that the acid treatment had had some chemical effect on the kerogen. To investigate the possibility of physical absorption, a known weight of Scottish shale oil, dissolved in acetone, was mixed into a paste with approximately ten times its weight of Stourbridge "mild" clay and the solvent allowed to evaporate slowly. After standing for one week, the mixture, which was hard and dry, was soxhlet-extracted with acetone; the solvent dissolved only 87 per cent. of the oil, the remainder being retained by the clay. The procedure was repeated using a sample of Stourbridge "strong" clay, with similar results, the percentage of oil retained being slightly higher. Thus the increase in the proportion of kerogen extracted from the de-ashed samples is probably due to part of the "soluble" material in the oil shales being physically absorbed on the mineral matter.

In order to determine whether the acid treatment of oil shales gave reproducible results, the process was carried out in duplicate on a sample of Amherst oil shale. The analyses of the two de-ashed samples, which are recorded in Table C, showed that, although the removal of the silicates had been accomplished to different extents, the compositions of the kerogens calculated from these results were substantially the same. Therefore it is unlikely that the reagents had had any chemical effect on the kerogen, as it is improbable that the organic matter would be attacked to the same degree in different experiments.

The acid treatment for de-ashing has been applied to a sample of South African torbanite, from Mooifontein 287 in the Ermelo district, and one of Kohat oil shale from the N.W.F.P. of India. In the case of these samples and the Amherst oil shale, the iron pyrites was removed by reduction with nascent hydrogen formed *in situ* by the addition of concentrated hydrochloric acid to an intimate mixture of the sample with zinc dust. The hydrogen sulphide evolved was absorbed in an ammoniacal cadmium chloride solution and the sulphur estimated volumetrically by the iodine and sodium thiosulphate method. Finally, the residue was thoroughly washed with dilute hydrochloric acid and a large volume of water, to remove the iron and zinc chlorides, dried and weighed. The analyses of these samples are given in Table D.

The small amounts of ash obtained by the combustion of the de-ashed South African and Kohat kerogens were bright red in colour, soluble in hydrochloric acid, and were practically pure ferric oxide. Treatment with zinc and hydrochloric acid and with nitric acid, sp. gr. 1·12, both

failed to dissolve the remaining iron, and since G. A. Cave (unpublished research) has shown that both the methods remove iron pyrites quantitatively, the iron cannot be present as sulphide. As all attempts to extract the iron failed and the repeated treatments had apparently no effect on the percentage of ferric oxide obtained on combustion, its presence is strongly presumptive evidence that the iron is directly combined with the organic matter and is, therefore, a constituent of the kerogens of South African torbanite and Kohat oil shale.

TABLE C.

Analysis of Amherst Oil Shale, Burma.

	Untreated Sample.		De-ashed Sample 1.		De-ashed Sample 2.	
	A, %.	B, %.	A, %.	B, %.	A, %.	B, %.
Carbon . .	40·95	73·1	73·35	77·47	74·76	77·46
Hydrogen .	6·14	11·0	10·46	10·11	10·77	11·16
Nitrogen .	0·55	1·0	1·23	1·31	1·21	1·25
Sulphur . .	0·82	1·4	0·75	0·79	0·79	0·81
" Oxygen " .	7·6	13·5	8·89	9·39	8·97	9·32
Mineral Matter	43·95	—	5·32	—	3·52	—
C/H ratio .		6·6		7·0		7·0
C/O ratio .		5·6		8·3		8·3

A = Composition as obtained by analysis.
B = Composition of kerogen calculated from A.

Examination of the compositions of the kerogens of the three samples of South African torbanite, two calculated from the analyses of the de-ashed samples prepared by Mr. Quass and the one given in Table D, show that they vary between very wide limits, particularly the oxygen values. On the other hand the compositions of the kerogens from four different seams of Scottish oil shales, recorded in Table VI page 236, are all very similar,

TABLE D.

Analysis of South African Torbanite and Kohat Oil Shale.

	South African.			Kohat.		
	A, %.	B, %.	C, %.	A, %.	B, %.	C, %.
Carbon . . .	42·76	78·72	79·75	8·60	71·32	72·58
Hydrogen . .	4·55	7·72	7·82	1·34	7·96	8·11
Nitrogen . .	0·91	1·54	1·56	0·18	1·31	1·34
Sulphur . .	0·32	1·20	1·22	0·55	0·80	0·81
" Oxygen " . .	6·4	9·52	9·65	4·0	16·86	17·16
Mineral Matter .	44·9	1·86	—	85·3	2·56	—
C/H ratio . .	9·4		10·2	6·4		9·0
C/O ratio . .	6·7		8·3	2·1		4·2

A = Analysis of original dry sample.
B = Analysis of de-ashed sample.
C = Composition of kerogen calculated from B.
Mineral matter = Ash on incineration plus carbon dioxide from carbonates.

and recent results from the de-ashing of three samples of Lower Dunnet oil shale, from Westwood, are in close agreement with those already reported. The differences in the analyses of the torbanite may be due to variations in the proportion of one particular source-material, which had a chemical composition markedly different from the average. Microscopic examination has revealed that in the organic matter of Scottish oil shales plant remains predominate, there being very few spore cases and algae, whereas in South African torbanite the vegetable debris is associated with large numbers of algal colonies. It is possible that differences in the ratio of algal bodies to general plant debris are responsible for the variations in the results obtained for the composition of the torbanite kerogen.

The very marked differences in the analyses of the kerogens as calculated from the results of determinations on untreated oil shales and the de-ashed samples are undoubtedly due to the effects of the water of hydration of the clays. It was realised from the first that this water was responsible for large errors in the composition of the organic matter and it was with the object of eliminating these errors that the isolation of the kerogen was attempted. In the de-ashing process employed at the Imperial College, the filtrates from the acid treatments were analysed and weight balances calculated, and no part of the kerogen could have been removed. Further, as is illustrated by Table E, the determination of carbon and hydrogen at each stage showed that the C/H ratio remained constant until the silicates were attacked.

TABLE E.

Carbon and Hydrogen on Middle Dunnet Oil Shale.

	Carbon, %.	Hydrogen, %.	C/H Ratio.
Dry sample . . .	12·98*	2·04	6·38
HCl treated . . .	15·08	2·37	6·35
HNO_3 treated . .	15·33	2·39	6·41
HF treated . . .	78·63	8·17	9·62

* Less carbon present as carbonate.

The additional results relating to the acid treatment for removing substantially all the mineral matter from oil shales indicate that the method is satisfactory. In the study of coals certain important relationships were developed from considerations of the ultimate analyses of a great many samples, *i.e.*, Ralston's [4] and Hickling's [5] diagrams, which showed the general continuity of the "peat ⟶ anthracite" series, and when the true compositions of a large number of oil shale kerogens have been obtained it may be possible to trace some parallel relationship for these materials.

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